An Abstract of the Thesis of

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Under the electric dipole approximation, second harmonic generation is forbidden by symmetry for centrosymmetric media. As a consequence, second harmonic radiation can only arise from a few atomic layers in the surface region where the symmetry is broken in the direction of the surface normal. Surface second harmonic generation (SSHG) can thus provide information about surfaces and surface phenomena.

The first part of this thesis deals with the development of the self-consistent microscopic field formulation of SSHG. The exact second harmonic field from the surface of a crystal is calculated using an incident plane wave, the polarizabilities $\alpha(\omega)$ and $\alpha(2\omega)$, and the second-order susceptibility $\beta(2\omega;\omega,\omega)$, all of which may vary with distance from the surface into the bulk. A self-consistent formulation in the Lorentz gauge has been used, including up to 100 discrete layers and a semi-infinite bulk with both long and short range dipolar interactions. The precise interpretation of SSHG measurements in terms of the local fields and susceptibilities requires this approach as opposed to the macroscopic formulations.

The second part of this thesis deals with experimental measurements of SSHG, including studies of the surface of the rutile (TiO_2) crystal and of thin films of amorphous

carbon (*a*-C:H). With the surface effect dominating the total SHG signal, SSHG provides the means to probe the adsorption and photodesorption of oxygen on the rutile (001) surface. On the other hand, the amorphous carbon films are found to be very photo-active. Second harmonic generation is accompanied by either photo-ablation or irreversible changes in the optical properties of the films.

Theory and Application of Optical Second Harmonic Generation on Dielectric Surfaces

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THEORY AND APPLICATION OF OPTICAL SECOND HARMONIC GENERATION ON DIELECTRIC SURFACES

CHAPTER I

INTRODUCTION

In second harmonic generation (SHG), matter responds to an incident optical wave in a nonlinear way such that an optical wave emerges at a frequency twice that of the incident wave. This process is forbidden under the electric dipole approximation for matter with inversion symmetry. In the surface region of a centrosymmetric medium, SHG is no longer forbidden because of the breaking of symmetry along the direction of the surface normal. Although SHG can still arise from the bulk by either electric dipole transition moments, the SHG due to the electric dipole transition moments from the surface provides at least a comparable signal level with that from the bulk. Hence, SHG becomes a sensitive technique in the study of surfaces and surface phenomena.

In surface studies, it is difficult to detect signals from a small number of surface atoms in the presence of a large number of bulk atoms. Many surface-sensitive techniques use electrons, atoms or ions as probing particles,¹ which need to have a low penetration depth to avoid a signal contribution from the bulk. Since these particles have to have a long mean free path to be able to strike and exit the sample and then reach the detector without colliding with other gas-phase molecules, the experiments are required to be performed in a high vacuum system. X-ray and ultraviolet photoelectron spectroscopies¹ are two common methods involving photons as the surface probes. SHG is uniquely capable of gathering the surface information under conditions ranging from ultra high vacuum to atmospheric environments with relatively low energy photons.

From the perspective of the surface atoms (molecules), in one direction there exist only identical atoms (molecules), while in the other direction there may be only a vacuum or a single layer of another type of atoms (molecules). This condition not only breaks the bulk symmetry but also creates a region where the local electric field is different from that of the bulk region. The local field is the microscopic field acting on the medium and is represented by the superposition of the external field and the induced dipole fields from the surrounding medium. It is the local field that the atoms (or molecules) respond to, linearly or nonlinearly. Thus, the interpretation of the interaction between the matter and an external field requires the knowledge of the local field in the medium. Since detecting the SHG from the surface region is our main interest, the surface local field calculation is a subject we have pursued in this study.

The local field calculation involves the summation over the field contributions from the surrounding medium. The basic difficulty of this summation problem is the slowness of convergence because of the 1/R dependency of the electric dipole field. The degree of difficulty can be greatly reduced if we are dealing with the summation over the sites of an infinite perfect lattice. Lattice sums occur in many problems of crystal physics, such as calculations of the lattice energy of ionic crystals, considerations of the stability of the various lattice types, and investigations of the electromagnetic, optical, or elastic properties of crystals. The summation recipe usually consists of the transformation of the lattice sum into a more rapidly converging form, *e.g.* the Fourier transform of a smooth function is a function which approaches zero rapidly for increasing argument. The essential mathematical technique in our approach to the lattice sum of the dipole fields was due to Ewald.² The method was originally developed on the basis of a three dimensional Fourier transform^{3,4} to deal with the bulk properties of the 3-D perfect crystal lattice. Motivated by the need to solve problems involving the geometry of a slab, Nijboer and de Wette⁵ modified the Ewald method and developed the planewise lattice sum which sums over the two dimensional lattice sites, with the help of the 2-D Fourier transform, and later treats the lattice sum of the third dimension (in the direction of surface normal) separately.

Under the framework of a planewise lattice sum Litzman⁶ formulated a microscopic theory of reflection and transmission of light by a dielectric slab by proposing that the induced dipole moments, which interacted with the retarded electromagnetic field, could be decomposed into an infinite number of dipole waves in the medium. The resulting formulae include both the effects known in the dynamical theory of X-ray diffraction as well as Snell's law and Fresnel's formulae for visible light. Poppe and Wijers *et al.*^{7,8} later developed a double cell technique to calculate the surface local field by matching a freely chosen surface layer to the underlying bulk described by Litzman's decomposed dipole waves. The technique is a local model based on the discrete dipole approach. They calculated the bulk and surface contributions to the anisotropic reflectance of the (110) surface of GaP and obtained results as good as the best delocalized treatments.⁷

Following the guidance of references 6, 7 and 8, we present a complete derivation of the microscopic treatment of the surface local field in Chapter II. After working out the algebraic details, there are discrepancies between our results and the previous works^{8,9} in the expressions of the lattice sum (see pages 20 and 22), although they are not significant in the numerical computations. Meanwhile, based on our numerical calculations, we found that the near fields of the induced dipole moments can not be ignored when considering the bulk contribution to the optical property of a dielectric medium. This conclusion is in contradiction to what has been stated by the other researchers.^{6,10} With the numerical results as well as an analytical argument, we

also show that the radiation damping of the electric dipole radiation has to be included in describing the medium response to an external field. The microscopic treatment of the discrete point dipole approach was put to a test when the numerical results of the local field in the medium and the reflected field in the vacuum were compared to the classical results of the Lorentz local field and Fresnel's formulae for reflection.

In Chapter III, we first review the argument that SHG is capable of providing surface information in the presence of the bulk background. Three models to obtain the analytical expressions of surface second harmonic generation (SSHG) are also discussed. We then go on to calculate SSHG using the complete microscopic treatment and the surface local field obtained in Chapter II.

The numerical calculation of SSHG in Chapter III is important to the measurements of the exact value of the nonlinear susceptibility $\beta(2\omega;\omega,\omega)$. These measurements require the careful calibrations of the signal conversion factors from materials of well known β . But the SSHG experiments we report in Chapter IV were not set up for this purpose. The primary goal of the experiments we have performed was to use SSHG to monitor the surface changes under the various environments. The calculations thus do not help in any way to interpret the observations in these experiments but will be essential to future studies.

The pulsed laser system and the experimental apparatus are introduced in section 4.1. The typical signal level of SSHG is also estimated. Examples of photon counting statistics are presented in section 4.1.4. In section 4.2, we report the SSHG observations of the surface phenomena of the rutile (TiO_2) crystal. We have paid special attention to the unique observation of the adsorption and photodesorption of oxygen on the rutile surface, which has been studied for years by other researchers¹¹ using other surface-sensitive techniques and much more energetic photons or electrons. Experimental results of the amorphous hydrogenated carbon (*a*-C:H) thin film are

summarized in section 4.3. So far as SSHG is concerned, the carbon film experiments are not successful because laser pulses change the film, not just the surface, properties. The temperature rise in the film due to heating of the laser pulse has been estimated using the thermal properties of the graphite and the quartz substrate. Photo-ablation and photo-induced changes in the presence of vacuum, oxygen, nitrogen and methanol vapor have been observed.

CHAPTER II

SURFACE LOCAL FIELD CALCULATION WITH DISCRETE POINT DIPOLE MODEL

In the point dipole model, the medium responds to an external field through the induced dipole moment of each unit cell of a crystal. The dipole moment is approximated as a local response so that the model is ideal for materials such as ionic solids and rare gas solids, in which the electrons are confined to the closed shells, and the weakly interacting molecular solids. The unit cell polarizability of these materials can be evaluated as a local quantity from theoretical calculations.¹² The nonlocal part of this response process is solely attributed to the dipolar interaction which will be treated explicitly in this study.

An induced dipole moment at lattice site *i* with unit cell polarizability tensor α_i is

$$\mathbf{p}(\mathbf{r}_{i},t) = \mathbf{\alpha}_{i} \cdot \mathbf{E}_{\text{loc}}(\mathbf{r}_{i},t) = \mathbf{\alpha}_{i} \cdot \left[\mathbf{E}_{0}e^{i\mathbf{k}\cdot\mathbf{r}_{i}-i\omega t} + \sum_{j\neq i}\mathbf{E}_{\text{dip},j}(\mathbf{r}_{i},t)\right], \quad (2.1)$$

where the local electric field is the superposition of the external field and the electric dipole field from all lattice sites in the system except itself. It is assumed that the external field is a monochromatic plane wave. Here we exclude the self-interaction term, but later we will consider the self-field¹³ in treating the dipole radiation, which is equivalent to including a radiation damping¹³ term in the polarizability, to prevent the solution of the dipole moment from diverging.

2.1 Electric Dipole Radiation

To describe the radiation from an electric dipole in vacuum, we start with the microscopic Maxwell equations:

$$\nabla \cdot \mathbf{E} = 4\,\pi\rho\,,\tag{2.2a}$$

$$\nabla \cdot \mathbf{B} = 0, \qquad (2.2b)$$

$$\nabla \times \mathbf{E} + \frac{1}{c} \dot{\mathbf{B}} = 0, \qquad (2.2c)$$

$$\nabla \times \mathbf{B} - \frac{1}{c} \dot{\mathbf{E}} = \frac{4\pi}{c} \mathbf{j}.$$
 (2.2d)

The equations are written in the Gaussian unit system. The charge density $p(\mathbf{r}, t)$ and the current density $\mathbf{j}(\mathbf{r}, t)$ in each cell are induced by the external field. From vector analysis of Eq.(2.2b) and Eq.(2.2c), there is a vector potential **A** and a scalar potential Φ satisfying

$$\mathbf{B} = \nabla \times \mathbf{A} \qquad \text{and} \qquad (2.3a)$$

$$\mathbf{E} = -\frac{1}{c}\dot{\mathbf{A}} - \nabla\Phi. \tag{2.3b}$$

These potential functions can be specified by the remaining Maxwell equations. Upon substituting Eq.(2.3a) and Eq.(2.3b) into Eq.(2.2a) and Eq.(2.2d), with the help of the vector identities $\nabla \times \nabla \times \equiv \nabla \nabla - \nabla^2$ and $\nabla \cdot \nabla \equiv \nabla^2$, we obtain

$$\nabla^{2}\mathbf{A} - \frac{1}{c^{2}}\ddot{\mathbf{A}} - \nabla\left(\nabla\cdot\mathbf{A} + \frac{1}{c}\dot{\mathbf{\Phi}}\right) = -\frac{4\pi}{c}\mathbf{j},$$
 (2.4a)

and
$$\nabla^2 \Phi - \frac{1}{c^2} \ddot{\Phi} + \frac{1}{c} \frac{\partial}{\partial t} \left(\nabla \cdot \mathbf{A} + \frac{1}{c} \dot{\Phi} \right) = -4\pi\rho.$$
 (2.4b)

There are four equations to solve for the four functions A and Φ , but Eq.(2.4a) and Eq.(2.4b) are not independent. If we apply the operator ∇ to Eq.(2.4a) and $\frac{1}{c}\frac{\partial}{\partial t}$ to

Eq.(2.4b), and then combine these two equations, the left hand side of the equation will be zero while the right hand side also is zero due to the continuity equation

$$\nabla \cdot \mathbf{j} + \dot{\boldsymbol{\rho}} = 0. \tag{2.5}$$

This means that one of the four equations is redundant, and one more condition has to be imposed in order to find **A** and Φ . One possibility is to use the so called "Lorentz condition",^{13,14,15}

$$\nabla \cdot \mathbf{A} + \frac{1}{\dot{c}} \dot{\mathbf{\Phi}} = 0, \qquad (2.6)$$

then Eqs.(2.4) become

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \ddot{\mathbf{A}} = -\frac{4\pi}{c} \mathbf{j}, \qquad (2.7a)$$

$$\nabla^2 \Phi - \frac{1}{c^2} \ddot{\Phi} = -4\pi\rho. \qquad (2.7b)$$

These inhomogeneous wave equations have solutions^{13,14,15}

$$\mathbf{A}(\mathbf{r},t) = \frac{1}{c} \int \frac{\mathbf{j}(\mathbf{r}', t - R / c)}{R} d\mathbf{v}', \qquad (2.8a)$$

$$\Phi(\mathbf{r},t) = \int \frac{\rho(\mathbf{r}',t-R/c)}{R} d\mathbf{v}', \qquad (2.8b)$$

where $R = |\mathbf{r} \cdot \mathbf{r}'|$ and the integration is to be carried throughout the whole space. These solutions are the retarded potentials of outgoing spherical waves. If we substitute the solutions of Eq.(2.8) into Eq.(2.6), it is obvious that the Lorentz condition is consistent with the equation of continuity. Since the current and charge densities are related in the same way as the vector and scalar potentials are related, we can now define a single source vector function P and a single vector potential function Z while they appear together in a single inhomogeneous wave equation. They are introduced by the relations

$$\mathbf{j} = \frac{\partial}{\partial t} \mathbf{P}, \qquad (2.9a)$$

$$\boldsymbol{\rho} = -\nabla \cdot \boldsymbol{P}, \qquad (2.9b)$$

and

$$\mathbf{A} = \frac{1}{c} \frac{\partial}{\partial t} \mathbf{Z}, \qquad (2.9c)$$

$$\Phi = -\nabla \cdot \mathbf{Z}.$$
 (2.9d)

Function Z is known as Hertz vector.^{14,15} Eq.(2.7) can be converted into

$$\nabla^2 \mathbf{Z} - \frac{1}{c^2} \ddot{\mathbf{Z}} = -4\pi \mathbf{P}, \qquad (2.10)$$

and the retarded solution of this wave equation is similar to that in Eq.(2.8),

$$\mathbf{Z}(\mathbf{r},t) = \int \frac{\mathbf{P}(\mathbf{r}', t - R / c)}{R} d\mathbf{v}'. \qquad (2.11)$$

When ρ , **j**, and **P** are induced by the external electromagnetic field in Eq.(2.1), their monochromatic nature can be represented by

$$\boldsymbol{P}(\mathbf{r}^{\prime},t) = \boldsymbol{P}(\mathbf{r}^{\prime})e^{-i\omega t}$$

When applying this to Eq.(2.11), we have

$$\mathbf{Z}(\mathbf{r},t) = e^{-i\omega t} \int \frac{\boldsymbol{P}(\mathbf{r}')e^{ikR}}{R} d\mathbf{v}', \qquad (2.12)$$

where $k = |\mathbf{k}| = \omega/c$. When $\frac{e^{ikR}}{R}$ is expressed in terms of a multipole expansion, the lowest order of the integral in Eq.(2.12) gives the electric dipole moment of this source distribution, and the Hertz vector becomes

$$\mathbf{Z}(\mathbf{r},t) = e^{-i\omega t} \frac{e^{ikR}}{R} \int \boldsymbol{P}(\mathbf{r}') d\mathbf{v}' = e^{-i\omega t} \frac{e^{ikR}}{R} \mathbf{p}(\mathbf{r}_0).$$
(2.13)

The electric dipole moment **p** is the same as that in Eq.(2.1), $R = |\mathbf{r} - \mathbf{r}_0|$ and \mathbf{r}_0 is the position of the point dipole moment.

The radiation field of the electric dipole moment is obtained by substituting Eq.(2.9c) and Eq.(2.9d) into Eq.(2.3b)

$$\mathbf{E}_{dip}\left(\mathbf{r},t\right) = -\frac{1}{c^{2}}\frac{\partial^{2}}{\partial t^{2}}\mathbf{Z} + \nabla\nabla\cdot\mathbf{Z} = (k^{2} + \nabla\nabla\cdot)e^{-i\omega t}\frac{e^{ikR}}{R}\mathbf{p}(\mathbf{r}_{0}),$$
$$\mathbf{E}_{dip}\left(\mathbf{r}\right) = (k^{2} + \nabla\nabla\cdot)\frac{e^{ikR}}{R}\mathbf{p}(\mathbf{r}_{0}).$$
(2.14)

or

2.2 Self-consistent Calculation

Consider a single crystal surface at the plane z = 0 (Fig. 2.1). An external field, $\mathbf{E}_0 e^{i\mathbf{k}\cdot\mathbf{r}}$, impinges upon the surface from the vacuum with an angle θ and wave vector $\mathbf{k} = (k^x, k^y, k^z) = (\mathbf{k}^{\parallel}, k^z)$. Each lattice site in the medium of the lower half-space is the center of a unit cell. With the result of Eq.(2.14), Eq.(2.1) can be rewritten as

$$\mathbf{p}(\mathbf{r}_{i}) = \boldsymbol{\alpha}_{i} \cdot \mathbf{E}_{\text{loc}}(\mathbf{r}_{i}) = \boldsymbol{\alpha}_{i} \cdot \left[\mathbf{E}_{0} e^{i\mathbf{k}\cdot\mathbf{r}_{i}} + \sum_{j\neq i} \mathbf{H}_{ij} \cdot \mathbf{p}(\mathbf{r}_{j})\right].$$
(2.15)

The tensor \mathbf{H}_{ij} represents the electric dipole field at site *i* from a dipole moment at site *j*, and its element, according to Eq.(2.14), is

$$\left(\mathbf{H}_{ij}\right)^{uv} = \left[\left(\partial_{u} \partial_{v} + k^{2} \delta_{uv} \right) \frac{\exp(ik|\mathbf{r} - \mathbf{r}_{j}|)}{|\mathbf{r} - \mathbf{r}_{j}|} \right]_{\mathbf{r}} = \mathbf{r}_{i}, \qquad (2.16)$$

where u, v = x, y, z. The position vector can be expressed in terms of the planar lattice structure (Fig. 2.2) by

$$\mathbf{r} = \mathbf{r}^{\parallel} + \mathbf{z}z \quad \text{and}$$

$$\mathbf{r}_{i,nm} = \mathbf{r}^{\parallel}_{i,nm} + \mathbf{z}z_i = \mathbf{r}^{\parallel}_i + \mathbf{s}_{nm} + \mathbf{z}z_i = \mathbf{r}_i + \mathbf{s}_{nm}, \quad (2.17)$$

where **z** is the unit vector in *z*-axis and *i* is index for the lattice planes parallel to the surface. \mathbf{r}_{i}^{I} describes the origin of the two dimensional lattice \mathbf{s}_{nm} of plane *i* with integers $n, m = -\infty, ..., -1, 0, 1, ..., \infty$.

$$\mathbf{s}_{nm} = n\mathbf{s}_{1} + m\mathbf{s}_{2} = a(n + \xi m, \zeta m, 0), \qquad (2.18)$$
$$\mathbf{s}_{1} = a(1, 0, 0),$$
$$\mathbf{s}_{2} = a(\xi, \zeta, 0),$$



Fig. 2.1 The surface coordinate system. Surface layers are labelled as i = 0, 1, ..., L. z is in the direction of surface normal. k is wave vector of the incident field. The index $m = 0, 1, ..., \infty$ is relevant only for the analysis of the semi-infinite medium. The rectangle indicates the scattering plane.



Fig. 2.2 Coordinate system of the *i*-th lattice plane. $\mathbf{r}_{i}^{\parallel}$ is on the plane.

and *a* is the lattice constant. The *x*-axis is chosen to be in the direction of the planar lattice vector \mathbf{s}_1 , and ϕ is the angle between the *x*-axis and the plane of incidence (Fig. 2.1). For the square lattice, we have $\xi = 0$ and $\zeta = 1$. Other possibilities of ξ and ζ provide the general basis vectors of the 2-D lattice. The non zero $\mathbf{r}^{\mathbf{I}}_i$ allows possible displacement between the lattice planes. The external field can now be written as $\mathbf{E}_0 e^{i\mathbf{k}\cdot\mathbf{r}_i} e^{i\mathbf{k}\cdot\mathbf{s}_{nm}}$. We assume that, in the surface region, the polarizability varies only layer by layer. Then the induced dipole moment within a lattice plane *i* has a simple phase relation, $\mathbf{p}(\mathbf{r}) = \mathbf{p}_i \exp(i\mathbf{k}^{\mathbf{I}}\cdot\mathbf{s}_{nm})$ where $\mathbf{p}_i = \mathbf{p}(\mathbf{r}_i)$, due to the translational symmetry. This allows the lattice sum of \mathbf{H}_{ij} to be performed in the planewise fashion and \mathbf{p}_i to be solved layer by layer self-consistently.

 \mathbf{p}_i in Eq.(2.15) becomes

$$\mathbf{p}_{i} = \boldsymbol{\alpha}_{i} \cdot \left[\mathbf{E}_{0} e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_{j=0} \sum_{n,m} \mathbf{H}_{ij} \cdot \mathbf{p}_{j} e^{i\mathbf{k}\cdot\mathbf{s}_{nm}} \right]_{\mathbf{r}=\mathbf{r}_{i}} = \boldsymbol{\alpha}_{i} \cdot \left[\mathbf{E}_{0} e^{i\mathbf{k}\cdot\mathbf{r}_{i}} + \sum_{j=0} \mathbf{F}_{ij} \cdot \mathbf{p}_{j} \right]. \quad (2.19)$$

The summation over *n*, *m* excludes the point (0,0) just for the case of i = j to prevent the self-interaction. The tensor \mathbf{F}_{ij} represents the electric dipole field at the 2-D lattice origin (n = m = 0) of plane *i* from all the dipole moments of plane *j*, and is defined by

$$(\mathbf{F}_{ij})^{uv} = [(\partial_{u}\partial_{v} + k^{2}\delta_{uv})S_{j}(\mathbf{r},\mathbf{k})]_{\mathbf{r}=\mathbf{r}_{i}}$$
$$= \left[(\partial_{u}\partial_{v} + k^{2}\delta_{uv})\sum_{n,m} \frac{\exp(ik|\mathbf{r} - \mathbf{r}_{j,nm}|)}{|\mathbf{r} - \mathbf{r}_{j,nm}|}e^{i\mathbf{k}\cdot\mathbf{s}_{nm}} \right]_{\mathbf{r}=\mathbf{r}_{i}}.$$
(2.20)

Once \mathbf{F}_{ij} is determined, Eq.(2.19) can be rearranged into

$$\sum_{j=0} \left[\boldsymbol{\alpha}_i^{-1} \boldsymbol{\delta}_{ij} - \mathbf{F}_{ij} \right] \cdot \mathbf{p}_j = \mathbf{E}_0 e^{i \mathbf{k} \cdot \mathbf{r}_i}, \qquad (2.21)$$

and \mathbf{p}_i can be solved exactly for a system of a finite number layers from this linear set of equations.

2.3 Planewise Lattice Sum

The two dimensional lattice sum of Eq.(2.20) converges poorly because of the slow decrease of 1/R. The Ewald method^{2,3,4,5,16} divides the lattice sum into a sum in the real space and a sum in the reciprocal space, the latter space being based on the Fourier transform of a perfect crystal structure. The real space sum takes into account the rapidly changing near field, and the low frequency components of the reciprocal space sum represent the slowly varying far field.

Using the integral identity (see Appendix A-1)

$$\frac{e^{ikR}}{R} = \frac{2}{\sqrt{\pi}} \int_{(0)}^{\infty} \exp\left(-R^2 t^2 + \frac{k^2}{4t^2}\right) dt, \qquad (2.22)$$

the function S_i defined in Eq.(2.20) is converted into

$$S_{j}(\mathbf{r},\mathbf{k}) = \frac{2}{\sqrt{\pi}} \sum_{n,m} e^{i\mathbf{k}\cdot\mathbf{s}_{nm}} \int_{(0)}^{\infty} \exp\left(-|\mathbf{r}-\mathbf{r}_{j,nm}|^{2} t^{2} + \frac{k^{2}}{4t^{2}}\right) dt. \quad (2.23)$$

According to Eq.(2.23), the sum over the two dimensional crystal lattice could converge rapidly for large values of the integration variable t. So the scheme is to choose a positive real parameter E such that the sum with the integal $E \rightarrow \infty$ converges sufficiently rapidly in the real lattice space. On the other hand, in order to perform the Fourier transformation of the lattice sum in Eq.(2.23), we assume the case of interaction between different lattice planes, *i.e.* $i \neq j$, so that the lattice point n = m = 0 is included in the summation. If i = j, then

$$S_{j}'(\mathbf{r},\mathbf{k}) = \frac{2}{\sqrt{\pi}} \sum_{n,m\neq 0} e^{i\mathbf{k}\cdot\mathbf{s}_{nm}} \int_{(0)}^{\infty} \exp\left(-|\mathbf{r}-\mathbf{r}_{j,nm}|^{2} t^{2} + \frac{k^{2}}{4t^{2}}\right) dt,$$

$$= S_{j}(\mathbf{r},\mathbf{k}) - \left[\frac{2}{\sqrt{\pi}} \int_{(0)}^{\infty} \exp\left(-r^{2}t^{2} + \frac{k^{2}}{4t^{2}}\right) dt\right]_{r \to 0}.$$
 (2.24)

2.3.1 Two Dimensional Reciprocal Space Sum

With Eqs.(2.17), Eq.(2.23) can be rearranged into

$$S_{j}(\mathbf{r},\mathbf{k}) = \frac{2}{\sqrt{\pi}} \exp[i\mathbf{k} \cdot (\mathbf{r}^{\parallel} - \mathbf{r}_{j}^{\parallel})]$$

$$\times \int_{(0)}^{\infty} \exp\left(-(z - z_{j})^{2} t^{2} + \frac{k^{2}}{4t^{2}}\right) \sum_{n,m} \exp[i\mathbf{k} \cdot (\mathbf{r}_{j,nm}^{\parallel} - \mathbf{r}^{\parallel}) - |\mathbf{r}^{\parallel} - \mathbf{r}_{j,nm}^{\parallel}|^{2} t^{2}] dt,$$

$$= \frac{2}{\sqrt{\pi}} \exp[i\mathbf{k} \cdot (\mathbf{r}^{\parallel} - \mathbf{r}_{j}^{\parallel})] \int_{(0)}^{\infty} \exp\left(-(z - z_{j})^{2} t^{2} + \frac{k^{2}}{4t^{2}}\right) f(\mathbf{r}^{\parallel}, t) dt. \quad (2.25)$$

Since $f(\mathbf{r}^{*}, t) = f(\mathbf{r}^{*} + \mathbf{s}_{nm}, t)$ in the last equation, it is periodic in the two dimensional lattice space, and we can expand it in a Fourier series:

$$f(\mathbf{r}^{\scriptscriptstyle \|},t) = \sum_{p,q} h(\mathbf{g}_{pq},t) \exp(i\mathbf{g}_{pq}\cdot\mathbf{r}^{\scriptscriptstyle \|}), \qquad (2.26)$$

where $p, q = -\infty, ..., -1, 0, 1, ..., \infty$ and $\mathbf{g}_{pq} = p\mathbf{g}_1 + q\mathbf{g}_2$ is the vector of a reciprocal lattice point. From Eq.(2.18) and the requirment³ $\mathbf{s}_i \cdot \mathbf{g}_j = 2\pi \delta_{ij}$ (*i*, *j* = 1, 2), we find that

$$\mathbf{g}_1 = \frac{2\pi}{a\zeta}(\zeta, -\xi, 0), \ \mathbf{g}_2 = \frac{2\pi}{a\zeta}(0, 1, 0), \text{ and } \mathbf{g}_{pq} = \frac{2\pi}{a\zeta}(p\zeta, q - p\xi, 0).$$

The Fourier component $h(\mathbf{g}_{pq}, t)$ is determined by multiplying both sides of Eq.(2.26) with $\exp(-i\mathbf{g}_{p'q'}\cdot\mathbf{r}^{\parallel})$ and integrating over the area of one planar unit cell.

$$\iint_{\substack{\text{one}\\\text{cell}}} f(\mathbf{r}^{"}, t) \exp(-i\mathbf{g}_{p'q'} \cdot \mathbf{r}^{"}) d\mathbf{r}^{"} = \sum_{p,q} h(\mathbf{g}_{pq}, t) \iint_{\substack{\text{one}\\\text{cell}}} \exp(i\mathbf{g}_{pq} \cdot \mathbf{r}^{"}) \exp(-i\mathbf{g}_{p'q'} \cdot \mathbf{r}^{"}) d\mathbf{r}^{"},$$
$$= \sum_{p,q} h(\mathbf{g}_{pq}, t) \delta_{pp'} \delta_{qq'} A.$$

The 2-D unit cell area is $A = a^2 \zeta$. The delta functions are the results of integrations of periodic functions over period. We now have

$$h(\mathbf{g}_{pq},t) = \frac{1}{A} \iint_{\substack{\text{one}\\\text{cell}}} f(\mathbf{r}^{\parallel},t) \exp(-i\mathbf{g}_{pq} \cdot \mathbf{r}^{\parallel}) d\mathbf{r}^{\parallel},$$

$$= \frac{1}{A} \iint_{\substack{\text{one}\\\text{cell}}} \sum_{n,m} \exp[i\mathbf{k} \cdot (\mathbf{r}_{j,nm}^{\#} - \mathbf{r}^{\#}) - |\mathbf{r}^{\#} - \mathbf{r}_{j,nm}^{\#}|^{2} t^{2}] \exp(-i\mathbf{g}_{pq} \cdot \mathbf{r}^{\#}) d\mathbf{r}^{\#},$$
$$= \frac{\exp(-i\mathbf{g}_{pq} \cdot \mathbf{r}_{j}^{\#})}{A} \iint \exp[-i(\mathbf{k}^{\#} + \mathbf{g}_{pq}) \cdot \mathbf{r}^{\#} - |\mathbf{r}^{\#}|^{2} t^{2}] d\mathbf{r}^{\#}.$$

The last equation is obtained by changing the integration variable $\mathbf{r}^{\parallel} \rightarrow (\mathbf{r}^{\parallel} + \mathbf{r}^{\parallel}_{j,nm})$ and the fact that $\mathbf{s}_{nm} \cdot \mathbf{g}_{pq} = 2\pi \times \text{integer}$. The integration is to be done over the whole two dimensional space due to the sum over n, m. By introducing a new vector $\mathbf{k}^{\parallel}_{pq} = \mathbf{k}^{\parallel} + \mathbf{g}_{pq}$, and with the integral identity in Appendix A-5:

$$\iint \exp\left(-i\mathbf{k}^{\parallel}\cdot\mathbf{r}^{\parallel}-r^{\parallel^{2}}t^{2}\right)\mathrm{d}\mathbf{r}^{\parallel}=\frac{\pi}{t^{2}}\exp\left(\frac{-k^{\parallel^{2}}}{4t^{2}}\right),$$

Eq.(2.26) becomes

$$f(\mathbf{r}^{\parallel},t) = \frac{\pi}{At^2} \sum_{p,q} \exp\left(\frac{-k_{pq}^{\parallel^2}}{4t^2}\right) \exp[i\mathbf{g}_{pq} \cdot (\mathbf{r}^{\parallel} - \mathbf{r}_j^{\parallel})].$$

Upon substituting the last equation into Eq.(2.25), we reach the desired result:

$$S_{j}(\mathbf{r},\mathbf{k}) = \frac{2\sqrt{\pi}}{A} \sum_{p,q} \exp[i\mathbf{k}_{pq}^{\parallel} \cdot (\mathbf{r}^{\parallel} - \mathbf{r}_{j}^{\parallel})] \int_{(0)}^{\infty} \exp\left(-(z - z_{j})^{2} t^{2} + \frac{\kappa_{pq}^{2}}{4t^{2}}\right) \frac{1}{t^{2}} dt, \quad (2.27)$$

where $\kappa_{pq} = \sqrt{k^2 - |\mathbf{k}_{pq}^{*}|^2}$. The sum in Eq.(2.27) over reciprocal lattice points converges rapidly not only for large values of the variable *t*, but also as $t \to 0$. This is because in the long wavelength limit $\lambda >> a$ and $k = 2\pi/\lambda << |\mathbf{g}_{pq}|$ if $(p,q) \neq (0,0)$, so we have

$$\mathbf{\kappa}_{00} = |k^z|$$
 and
 $\mathbf{\kappa}_{pq} = i|\mathbf{\kappa}_{pq}|$ for $(p,q) \neq (0,0)$. (2.28)

Furthermore, by applying the integral identity from Appendix A-2,

$$2i\frac{e^{ikr}}{k} = \frac{2}{\sqrt{\pi}}\int_{(0)}^{\infty} \exp\left(-r^2t^2 + \frac{k^2}{4t^2}\right)\frac{1}{t^2}dt,$$

to Eq.(2.27), we have

$$S_{j}(\mathbf{r},\mathbf{k}) = \frac{2\pi i}{A} \sum_{p,q} \exp[i\mathbf{k}_{pq}^{\parallel} \cdot (\mathbf{r}^{\parallel} - \mathbf{r}_{j}^{\parallel})] \frac{\exp(i\kappa_{pq}|z - z_{j}|)}{\kappa_{pq}}.$$

The planar electric dipole transformation tensor \mathbf{F}_{ij} ($i \neq j$) can be obtained by applying the operator in Eq.(2.20) to the last equation, and the result is

$$(\mathbf{F}_{ij})^{uv}(\mathbf{k}) = \frac{2\pi i}{A} \sum_{p,q} \frac{-k_{pq}^{u} k_{pq}^{v} + k^{2} \delta_{uv}}{\kappa_{pq}} \exp[i\mathbf{k}_{pq} \cdot (\mathbf{r}_{i} - \mathbf{r}_{j})], \qquad (2.29)$$

where

$$k_{pq}^{x} = k^{x} + g_{pq}^{x},$$
 $k_{pq}^{y} = k^{y} + g_{pq}^{y},$ and $k_{pq}^{z} = \kappa_{pq} \frac{|z_{i} - z_{j}|}{(z_{i} - z_{j})}.$

The sum in Eq.(2.29) converges due to the factor $\exp(i\kappa_{pq}|z_i - z_j|)$ and Eq.(2.28). Rapidity of the convergency depends on the distance between two planes involved. On the other hand, as the distance $|z_i - z_j|$ increases, the short range part of the dipolar interaction between planes, represented by the sum of $(p,q) \neq (0,0)$ in tensor \mathbf{F}_{ij} $(i \neq j)$, decreases exponentially, while the long range part of the interaction, which is the dc term in the Fourier series (p, q = 0), gives a traveling wave with wave vector $\pm k^{z}$.

2.3.2 Lattice Sum in the Real and Reciprocal Spaces

In the long wavelength limit, *e.g.* photon energy of 2.0 eV and a lattice constant of 2.5 Angstroms ($ka \approx 2\pi/2480$), most of the sums in Eq.(2.29) converges up to seven digits precision with $|p| + |q| \le 3$. But for $|z_i - z_j| \le a$, the convergence slows down drastically, and we have to bring in Eq.(2.23) to combine with Eq.(2.27) to increase the computational efficiency. As in the previous discussion, Eq.(2.23) is efficient for large values of the integration variable *t*, while Eq.(2.27) is good for small values of *t*. By choosing a real parameter *E*, the function $S_i(\mathbf{r}, \mathbf{k})$ can be separated into two parts:

$$S_i(\mathbf{r},\mathbf{k}) = S_i^{\prime}(\mathbf{r},\mathbf{k}) + S_i^{\prime\prime}(\mathbf{r},\mathbf{k}),$$

with

$$S_{j}^{T}(\mathbf{r},\mathbf{k}) = \frac{2}{\sqrt{\pi}} \sum_{n,m} e^{i\mathbf{k}\cdot\mathbf{s}_{nm}} \int_{E}^{\infty} \exp\left(-|\mathbf{r}-\mathbf{r}_{j,nm}|^{2} t^{2} + \frac{k^{2}}{4t^{2}}\right) dt, \quad (2.30)$$

and
$$S_{j}^{II}(\mathbf{r},\mathbf{k}) = \frac{2\sqrt{\pi}}{A} \sum_{p,q} \exp[i\mathbf{k}_{pq}^{\#} \cdot (\mathbf{r}^{\#} - \mathbf{r}_{j}^{\#})] \int_{(0)}^{E} \exp\left(-(z - z_{j})^{2} t^{2} + \frac{\kappa_{pq}^{2}}{4t^{2}}\right) \frac{1}{t^{2}} dt.$$
 (2.31)

Before applying the differential operator in Eq.(2.20) to both functions, we convert the integrals in the functions into the complementary error functions with complex variables. Using the integal identity in Appendix A-3

$$\frac{2}{\sqrt{\pi}}\int_{E}^{\infty}\exp\left(-r^{2}t^{2}+\frac{k^{2}}{4t^{2}}\right)dt=\frac{1}{2r}\left[e^{ikr}\operatorname{erfc}\left(rE+\frac{ik}{2E}\right)+c.c.\right],$$

Eq.(2.30) becomes

$$S_{j}^{I}(\mathbf{r},\mathbf{k}) = \frac{1}{2} \sum_{n,m} \frac{e^{i\mathbf{k}\cdot\mathbf{s}_{nm}}}{|\mathbf{r}-\mathbf{r}_{j,nm}|} \left[e^{ik|\mathbf{r}-\mathbf{r}_{j,nm}|} \operatorname{erfc}(|\mathbf{r}-\mathbf{r}_{j,nm}|E + \frac{ik}{2E}) + e^{-ik|\mathbf{r}-\mathbf{r}_{j,nm}|} \operatorname{erfc}(|\mathbf{r}-\mathbf{r}_{j,nm}|E - \frac{ik}{2E}) \right]. \quad (2.32)$$

Also using the integal identity in Appendix A-4

$$\frac{2}{\sqrt{\pi}}\int_{(0)}^{E}\exp\left(-r^{2}t^{2}+\frac{k^{2}}{4t^{2}}\right)\frac{\mathrm{d}t}{t^{2}}=\frac{-1}{ik}\left[e^{ikr}\operatorname{erfc}\left(-rE-\frac{ik}{2E}\right)+e^{-ikr}\operatorname{erfc}\left(rE-\frac{ik}{2E}\right)\right],$$

Eq.(2.31) becomes

$$S_{j}^{II}(\mathbf{r},\mathbf{k}) = \frac{i\pi}{A} \sum_{p,q} \frac{\exp[i\mathbf{k}_{pq}^{\parallel} \cdot (\mathbf{r}^{\parallel} - \mathbf{r}_{j}^{\parallel})]}{\kappa_{pq}} \left[e^{i\kappa_{pq}|z-z_{j}|} \operatorname{erfc}\left(-|z-z_{j}|E - \frac{i\kappa_{pq}}{2E}\right) + e^{-i\kappa_{pq}|z-z_{j}|} \operatorname{erfc}\left(|z-z_{j}|E - \frac{i\kappa_{pq}}{2E}\right) \right]. \quad (2.33)$$

The complementary error function is introduced by $\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} \exp(-t^2) dt$.

Considering an integral function $f(x) = \int_{x}^{\infty} h'(t) dt = [h(t)]_{t=x}^{t=\infty}$, we have the derivative of

the function as $\frac{df(x)}{dx} = -\frac{dh(x)}{dx}$. So the derivative of a complementary error function is just $-\frac{2}{\sqrt{\pi}} \exp(-x^2)$.

We first take the first derivative of Eq.(2.32):

$$\begin{split} \partial_{\nu} S_{j}^{i} &= \frac{1}{2} \sum_{n,m} \left\{ \frac{e^{i\mathbf{k}\cdot\mathbf{s}_{mn}}}{|\mathbf{r} - \mathbf{r}_{j,nm}|^{3}} [-(\nu - r_{j,nm}^{\nu})] \right\} \left[e^{i\mathbf{k}|\mathbf{r} - \mathbf{r}_{j,nm}|} \operatorname{erfc}(|\mathbf{r} - \mathbf{r}_{j,nm}|E + \frac{ik}{2E}) + c.c. \right] + \frac{e^{i\mathbf{k}\cdot\mathbf{s}_{mn}}}{|\mathbf{r} - \mathbf{r}_{j,nm}|} \\ &\times \left\{ \frac{ik(\nu - r_{j,nm}^{\nu})}{|\mathbf{r} - \mathbf{r}_{j,nm}|} e^{i\mathbf{k}|\mathbf{r} - \mathbf{r}_{j,nm}|} \operatorname{erfc}(|\mathbf{r} - \mathbf{r}_{j,nm}|E + \frac{ik}{2E}) + e^{i\mathbf{k}|\mathbf{r} - \mathbf{r}_{j,nm}|} \left(-\frac{2}{\sqrt{\pi}} \right) \frac{(\nu - r_{j,nm}^{\nu})}{|\mathbf{r} - \mathbf{r}_{j,nm}|} \right. \\ &\times E \exp[-(|\mathbf{r} - \mathbf{r}_{j,nm}|E + \frac{ik}{2E})^{2}] + c.c. \right\}, \\ &= \frac{1}{2} \sum_{n,m} e^{i\mathbf{k}\cdot\mathbf{s}_{nm}} \left\{ \frac{-(\nu - r_{j,nm}^{\nu})}{|\mathbf{r} - \mathbf{r}_{j,nm}|^{3}} \left[e^{i\mathbf{k}|\mathbf{r} - \mathbf{r}_{j,nm}|} \operatorname{erfc}(|\mathbf{r} - \mathbf{r}_{j,nm}|E + \frac{ik}{2E}) + c.c. \right] + \frac{(\nu - r_{j,nm}^{\nu})}{|\mathbf{r} - \mathbf{r}_{j,nm}|^{2}} \\ &\times \left[ike^{i\mathbf{k}|\mathbf{r} - \mathbf{r}_{j,nm}|^{3}} \operatorname{erfc}(|\mathbf{r} - \mathbf{r}_{j,nm}|E + \frac{ik}{2E}) - \frac{2E}{\sqrt{\pi}} \operatorname{exp}(-|\mathbf{r} - \mathbf{r}_{j,nm}|^{2}E^{2} + \frac{k^{2}}{4E^{2}}) + c.c. \right] \right\}. \end{split}$$

When the operator in Eq.(2.20) is applied, we find that

$$(\partial_{u}\partial_{v} + k^{2}\delta_{uv})S_{j}^{l} = \frac{1}{2}\sum_{n,m}e^{i\mathbf{k}\cdot\mathbf{s}_{nm}}\left\{\left[\frac{3(v-r_{j,nm}^{v})(u-r_{j,nm}^{u})}{|\mathbf{r}-\mathbf{r}_{j,nm}|^{5}} - \frac{\delta_{uv}}{|\mathbf{r}-\mathbf{r}_{j,nm}|^{3}} + \frac{k^{2}\delta_{uv}}{|\mathbf{r}-\mathbf{r}_{j,nm}|}\right]\right\}$$

$$\times \left[e^{ik|\mathbf{r}-\mathbf{r}_{j,nm}|}e^{i\mathbf{k}|\mathbf{r}-\mathbf{r}_{j,nm}|^{3}} + \frac{ik}{2E}\right] + c.c.\right] - \frac{(v-r_{j,nm}^{v})}{|\mathbf{r}-\mathbf{r}_{j,nm}|^{3}}\left[\frac{ik(u-r_{j,nm}^{u})}{|\mathbf{r}-\mathbf{r}_{j,nm}|}e^{i\mathbf{k}|\mathbf{r}-\mathbf{r}_{j,nm}|}e^{i\mathbf{k}|\mathbf{r}-\mathbf{r}_{j,nm}|^{3}} + \frac{k^{2}\delta_{uv}}{|\mathbf{r}-\mathbf{r}_{j,nm}|}E + \frac{ik}{2E}\right]$$

$$-e^{ik|\mathbf{r}-\mathbf{r}_{j,nm}|^{2}}\frac{2E}{\sqrt{\pi}}\frac{(u-r_{j,nm}^{u})}{|\mathbf{r}-\mathbf{r}_{j,nm}|}exp[-(|\mathbf{r}-\mathbf{r}_{j,nm}|E + \frac{ik}{2E})^{2}] + c.c.\right] + \left[\frac{-2(v-r_{j,nm}^{v})(u-r_{j,nm}^{u})}{|\mathbf{r}-\mathbf{r}_{j,nm}|^{4}} + \frac{\delta_{uv}}{|\mathbf{r}-\mathbf{r}_{j,nm}|^{2}}\right]$$

$$\times \left[ike^{ik|\mathbf{r}-\mathbf{r}_{j,nm}|}erfc(|\mathbf{r}-\mathbf{r}_{j,nm}|E + \frac{ik}{2E}) - \frac{2E}{\sqrt{\pi}}exp(-|\mathbf{r}-\mathbf{r}_{j,nm}|^{2}E^{2} + \frac{k^{2}}{4E^{2}}) + c.c.\right] + \frac{(v-r_{j,nm}^{v})}{|\mathbf{r}-\mathbf{r}_{j,nm}|^{2}}\right]$$

$$\times \left[\frac{(ik)^{2} (u - r_{j,nm}^{u})}{|\mathbf{r} - \mathbf{r}_{j,nm}|} e^{ik|\mathbf{r} - \mathbf{$$

When the last equation is evaluated at $\mathbf{r} = \mathbf{r}_i$, then

$$\begin{aligned} (\mathbf{F}_{ij}^{I})^{uv} &= \frac{1}{2} \sum_{n,m} e^{i\mathbf{k} \cdot \mathbf{s}_{nm}} \left\{ \left[e^{ik\mathbf{r}_{i} - \mathbf{r}_{i,nm}} erfc(|\mathbf{r}_{i} - \mathbf{r}_{j,nm}|E + \frac{ik}{2E}) \right] \left[\frac{3(r_{i}^{v} - r_{j,nm}^{v})(r_{i}^{u} - r_{j,nm}^{u})}{|\mathbf{r}_{i} - \mathbf{r}_{j,nm}|^{5}} - \frac{\delta_{uv}}{|\mathbf{r}_{i} - \mathbf{r}_{j,nm}|^{3}} \right] \\ &- \frac{3ik(r_{i}^{v} - r_{j,nm}^{v})(r_{i}^{u} - r_{j,nm}^{u})}{|\mathbf{r}_{i} - \mathbf{r}_{j,nm}|^{4}} + \frac{(ik)^{2}(r_{i}^{v} - r_{j,nm}^{v})(r_{i}^{u} - r_{j,nm}^{u})}{|\mathbf{r}_{i} - \mathbf{r}_{j,nm}|^{3}} + \frac{ik\delta_{uv}}{|\mathbf{r}_{i} - \mathbf{r}_{j,nm}|^{2}} + \frac{k^{2}\delta_{uv}}{|\mathbf{r}_{i} - \mathbf{r}_{j,nm}|} \right] \\ &+ \left[\frac{2E}{\sqrt{\pi}} \exp(-|\mathbf{r}_{i} - \mathbf{r}_{j,nm}|^{2}|E^{2} + \frac{k^{2}}{4E^{2}}) \right] \left[\frac{3(r_{i}^{v} - r_{j,nm}^{v})(r_{i}^{u} - r_{j,nm}^{u})}{|\mathbf{r}_{i} - \mathbf{r}_{j,nm}|^{4}} - \frac{ik(r_{i}^{v} - r_{j,nm}^{v})(r_{i}^{u} - r_{j,nm}^{u})}{|\mathbf{r}_{i} - \mathbf{r}_{j,nm}|^{3}} \right] \\ &+ \frac{2E^{2}(r_{i}^{v} - r_{j,nm}^{v})(r_{i}^{u} - r_{j,nm}^{u})}{|\mathbf{r}_{i} - \mathbf{r}_{j,nm}|^{2}} + c.c. \right\}. \end{aligned}$$

When applying the operator in Eq.(2.20) to Eq.(2.33), we examine the result in three different cases.

Case I:
$$u = v = z$$
, with $k_{pq}^z = \kappa_{pq} \frac{|z_i - z_j|}{(z_i - z_j)}$ and $E^z = E \frac{|z_i - z_j|}{(z_i - z_j)}$. The tensor element is

$$(\mathbf{F}_{ij}^{II})^{zz} = \frac{\pi i}{A} \sum_{p,q} \frac{\exp[i\mathbf{k}_{pq}^{\parallel} \cdot (\mathbf{r}_{i}^{\parallel} - \mathbf{r}_{j}^{\parallel})]}{\kappa_{pq}} \left\{ (ik_{pq}^{z})^{2} e^{i\kappa_{pq}|z-z_{j}|} \operatorname{erfc}(-|z-z_{j}|E - \frac{i\kappa_{pq}}{2E}) + e^{i\kappa_{pq}|z-z_{j}|} \right\}$$

$$\times \frac{2E^{z}}{\sqrt{\pi}} \exp[-(-|z_{i}-z_{j}|E-\frac{i\kappa_{pq}}{2E})^{2}][2ik_{pq}^{z}+2E^{z}(-|z_{i}-z_{j}|E-\frac{i\kappa_{pq}}{2E})]+(ik_{pq}^{z})^{2}e^{-i\kappa_{pq}|z-z_{j}|}$$

$$\times \operatorname{erfc}(|z-z_{j}|E - \frac{i\kappa_{pq}}{2E}) - e^{-i\kappa_{pq}|z-z_{j}|} \frac{2E^{z}}{\sqrt{\pi}} \exp[-(|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}]][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}]][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}]][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}]][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}]]][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}]]][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}]]][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}]]]][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}]]]][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}]]]][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}]]]][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}]]]]][-2ik_{pq}^{z} - (|z_{i}-z_{j}|E - \frac{i\kappa_{pq}}{2E})^{2}]]]]]]$$

$$-\frac{i\kappa_{pq}}{2E})2E^{z}]+k^{2}\left[e^{i\kappa_{pq}|z-z_{j}|}\operatorname{erfc}\left(-|z-z_{j}|E-\frac{i\kappa_{pq}}{2E}\right)+e^{-i\kappa_{pq}|z-z_{j}|}\operatorname{erfc}\left(|z-z_{j}|E-\frac{i\kappa_{pq}}{2E}\right)\right]\right\},$$

$$= \frac{\pi i}{A} \sum_{p,q} \frac{\exp[i\mathbf{k}_{pq}^{\parallel} \cdot (\mathbf{r}_{i}^{\parallel} - \mathbf{r}_{j}^{\parallel})]}{\kappa_{pq}} \left\{ (-\kappa_{pq}^{2} + k^{2})(\Delta_{pq}^{+} + \Delta_{pq}^{-}) + \frac{2}{\sqrt{\pi}} \exp(-|z_{i} - z_{j}|^{2} E^{2} + \frac{\kappa_{pq}^{2}}{4E^{2}}) \times [2ik_{pq}^{z} E^{z} - ik_{pq}^{z} E^{z} - 2|z_{i} - z_{j}|E^{3} + 2ik_{pq}^{z} E^{z} - ik_{pq}^{z} E^{z} + 2|z_{i} - z_{j}|E^{3}] \right\},$$

$$= \frac{\pi i}{A} \sum_{p,q} e^{i\kappa_{pq}^{\parallel} \cdot (\mathbf{r}_{i}^{\parallel} - \mathbf{r}_{j}^{\parallel})} \left\{ \frac{(k^{2} - \kappa_{pq}^{2})}{\kappa_{pq}} (\Delta_{pq}^{+} + \Delta_{pq}^{-}) + \frac{4iE}{\sqrt{\pi}} \exp(-|z_{i} - z_{j}|^{2} E^{2} + \frac{\kappa_{pq}^{2}}{4E^{2}}) \right\}, \quad (2.35)$$

where $\Delta_{pq}^{+} \equiv e^{i\kappa_{pq}|z-z_j|} \operatorname{erfc}(-|z-z_j|E-\frac{i\kappa_{pq}}{2E})$, and $\Delta_{pq}^{-} \equiv e^{-i\kappa_{pq}|z-z_j|} \operatorname{erfc}(|z-z_j|E-\frac{i\kappa_{pq}}{2E})$.

Case II: $u \neq z$ and v = z,

$$(\mathbf{F}_{ij}^{II})^{uz} = (\mathbf{F}_{ij}^{II})^{zu} = \frac{\pi i}{A} \sum_{p,q} e^{i\mathbf{k}_{pq}^{u} \cdot (\mathbf{r}_{i}^{u} - \mathbf{r}_{j}^{u})} \frac{-k_{pq}^{u} k_{pq}^{z}}{\kappa_{pq}} (\Delta_{pq}^{+} - \Delta_{pq}^{-}).$$
(2.36)

Case III: $u \neq z$ and $v \neq z$,

$$(\mathbf{F}_{ij}^{II})^{uv} = \frac{\pi i}{A} \sum_{p,q} e^{i\mathbf{k}_{pq}^{u} \cdot (\mathbf{r}_{i}^{u} - \mathbf{r}_{j}^{u})} \frac{k^{2} \delta_{uv} - k_{pq}^{u} k_{pq}^{v}}{\kappa_{pq}} (\Delta_{pq}^{+} + \Delta_{pq}^{-}).$$
(2.37)

Equations (2.34, 2.35, 2.36, and 2.37) can all converge rapidly because the complementary error functions drop to zero drastically as the arguments approach unity. The Ewald cut-off parameter has been chosen to be on the order of the inverse lattice constant to maintain balance between aE for Eq.(2.34) and 1/(aE) for the reciprocal lattice sums. Numerical evaluation of the complementary error function with complex argument is discussed in Appendix A-6. The expressions we obtain here mostly agree with the results by other groups^{8,9} except that we have an extra term:

$$-\frac{ik(r_i^v - r_{j,nm}^v)(r_i^u - r_{j,nm}^u)}{|\mathbf{r}_i - \mathbf{r}_{j,nm}|^3} \left[\frac{2E}{\sqrt{\pi}} \exp(-|\mathbf{r}_i - \mathbf{r}_{j,nm}|^2 E^2 + \frac{k^2}{4E^2})\right] \text{ in Eq.(2.34), although}$$

this will not affect the numerical outcome since this term is canceled by its own complex conjugate. It might have just been ignored without explanation because of its lack of contribution.

The tensor describing the electric dipole field from all the dipole moments of the lattice plane containing the point of interest, *i.e.* i = j, is C. We have to go back to Eq.(2.24) to delete the self-interaction term from the contribution for n = m = 0. With the Ewald cut-off parameter, we rewrite Eq.(2.24) as

$$S_{j}' = S_{j}' - \left[\frac{2}{\sqrt{\pi}}\int_{E}^{\infty} \exp\left(-r^{2}t^{2} + \frac{k^{2}}{4t^{2}}\right)dt\right]_{r \to 0} + S_{j}'' - \left[\frac{2}{\sqrt{\pi}}\int_{(0)}^{E} \exp\left(-r^{2}t^{2} + \frac{k^{2}}{4t^{2}}\right)dt\right]_{r \to 0}$$

The first integral can be eliminated directly from the real lattice sum in Eq.(2.30) and Eq.(2.32) by excluding the term n = m = 0. The second integral, which has been incorporated in the reciprocal lattice sum of Eq.(2.31) and Eq.(2.33), has to be treated through a polynomial expansion of $\exp(-r^2t^2)$. Define a tensor **D** as

$$\mathbf{D}^{uv} = -\frac{2}{\sqrt{\pi}} \left[(\partial_u \partial_v + k^2 \delta_{uv}) \int_{(0)}^{E} \exp\left(-r^2 t^2 + \frac{k^2}{4t^2}\right) dt \right]_{r \to 0} = \mathbf{D}_l^{uv} + \mathbf{D}_{ll}^{uv}.$$

Now, each element of C is

$$\mathbf{C}^{uv} = (\mathbf{F}_{ii}^{I})^{uv} + (\mathbf{F}_{ii}^{II})^{uv} + \mathbf{D}^{uv}, \qquad (2.38)$$

where \mathbf{F}_{ii}^{T} is to be evaluated with Eq.(2.34) without the lattice point n = m = 0. Continuing with the calculation of **D**,

$$\mathbf{D}_{I}^{uv} = -\frac{2}{\sqrt{\pi}} \left[(\partial_{u} \partial_{v}) \int_{(0)}^{E} \exp\left(-r^{2}t^{2} + \frac{k^{2}}{4t^{2}}\right) dt \right]_{r \to 0},$$

$$= -\frac{2}{\sqrt{\pi}} \left[(\partial_{u} \partial_{v}) \int_{(0)}^{E} (1 - r^{2}t^{2} + \frac{r^{4}t^{4}}{2!} - \frac{r^{6}t^{6}}{3!} + \cdots) \exp\left(\frac{k^{2}}{4t^{2}}\right) dt \right]_{r \to 0}.$$

With $r^2 = x^2 + y^2 + z^2$ and u, v = x, y, z, we have the following derivatives of the polynomials: $\partial_v r^2 = 2v$, $\partial_v r^4 = 2r^2 \partial_v r^2$, and $\partial_v r^6 = 3r^4 \partial_v r^2$. When applying these formulas to the last equation, the derivation continues with

$$\mathbf{D}_{I}^{uv} = -\frac{2}{\sqrt{\pi}} \left[(\partial_{u})(-2v) \int_{(0)}^{E} (t^{2} - \frac{2r^{2}t^{4}}{2!} + \frac{3r^{4}t^{6}}{3!} - \cdots) \exp\left(\frac{k^{2}}{4t^{2}}\right) dt \right]_{r \to 0},$$

$$= \frac{2}{\sqrt{\pi}} \left[2\delta_{uv} \int_{(0)}^{E} (t^{2} - \frac{2r^{2}t^{4}}{2!} + \cdots) \exp\left(\frac{k^{2}}{4t^{2}}\right) dt + 2v \int_{(0)}^{E} (0 - 2ut^{4} + \cdots) \exp\left(\frac{k^{2}}{4t^{2}}\right) dt \right]_{r \to (0)}$$
$$= \delta_{uv} \frac{2}{\sqrt{\pi}} \left[2\int_{(0)}^{E} t^{2} \exp\left(\frac{k^{2}}{4t^{2}}\right) dt \right]. \text{ Integration by parts,}$$
$$\mathbf{D}_{I}^{uv} = \delta_{uv} \frac{2}{\sqrt{\pi}} \left[2\exp\left(\frac{k^{2}}{4t^{2}}\right) \frac{t^{3}}{3} \Big|_{t=0}^{t=E} - 2\int_{(0)}^{E} \frac{t^{3}}{3} \exp\left(\frac{k^{2}}{4t^{2}}\right) (\frac{-2t^{-3}k^{2}}{4}) dt \right].$$

We now evaluate the second part of the tensor, which is

$$\mathbf{D}_{II}^{uv} = -\frac{2}{\sqrt{\pi}} \left[k^2 \delta_{uv} \int_{(0)}^{E} \exp\left(-r^2 t^2 + \frac{k^2}{4t^2}\right) dt \right]_{r \to 0} = -\delta_{uv} \frac{2}{\sqrt{\pi}} k^2 \int_{(0)}^{E} \exp\left(\frac{k^2}{4t^2}\right) dt.$$

Tensor D turns out to be diagonal. After combining the last two equations, it becomes

$$\mathbf{D}^{uv} = \delta_{uv} \frac{2}{\sqrt{\pi}} \left[\frac{2E^3}{3} \exp\left(\frac{k^2}{4E^2}\right) + \left(\frac{k^2}{3} - k^2\right) \int_{(0)}^{E} \exp\left(\frac{k^2}{4t^2}\right) dt \right],$$

$$= \delta_{uv} \frac{2}{\sqrt{\pi}} \left\{ \frac{2E^3}{3} \exp\left(\frac{k^2}{4E^2}\right) - \frac{2k^2}{3} \left[\int_{(0)}^{E} t \frac{k^2}{2t^3} \exp\left(\frac{k^2}{4t^2}\right) dt + t \exp\left(\frac{k^2}{4t^2}\right) \right]_{t=0}^{t=E} \right\},$$

$$= \delta_{uv} \frac{4E}{3\sqrt{\pi}} (E^2 - k^2) \exp\left(\frac{k^2}{4E^2}\right) - \delta_{uv} \frac{k^4}{3} \frac{2}{\sqrt{\pi}} \int_{(0)}^{E} \frac{1}{t^2} \exp\left(\frac{k^2}{4t^2}\right) dt.$$

Using the integral identity in Appendix A-4 (taking r = 0), we have the final expression:

$$\mathbf{D}^{uv} = \delta_{uv} \frac{4E}{3\sqrt{\pi}} (E^2 - k^2) \exp\left(\frac{k^2}{4E^2}\right) - \delta_{uv} \frac{2ik^3}{3} \operatorname{erfc}(-\frac{ik}{2E}).$$
(2.39)

Eq.(2.39) is compared with the results from three other groups:

(I) Poppe *et al.*⁸ reported that

$$\mathbf{D}^{uv} = \delta_{uv} \frac{4E}{3\sqrt{\pi}} (k^2 - E^2) \exp\left(\frac{k^2}{4E^2}\right) + \delta_{uv} \frac{2ik^3}{3} \operatorname{erfc}(\frac{ik}{2E}),$$

which differs from our result by an over all minus sign and another minus sign for the argument of the complementary error function. Note that $\operatorname{erfc}(-x) = 2 - \operatorname{erfc}(x)$. It is not clear how they evaluated the tensor for the limit $r \to 0$. The differences could be just printing errors.

(II) Litzman and Dub⁹ reported the expression

$$\mathbf{D}^{\mu\nu} = \delta_{\mu\nu} \left\{ \frac{4\pi}{3} \left(\frac{E}{\sqrt{\pi}} \right)^3 \left[(1 + \frac{k^2}{2E^2}) \exp\left(\frac{k^2}{4E^2}\right) - 2\sqrt{\pi} \left(\frac{ik}{2E}\right)^3 \operatorname{erf}\left(\frac{ik}{2E}\right) \right] - \frac{2ik^3}{3} \right\}$$
$$= \delta_{\mu\nu} \left\{ \frac{4E}{3\sqrt{\pi}} \left(E^2 + \frac{k^2}{2} \right) \exp\left(\frac{k^2}{4E^2}\right) - \frac{2ik^3}{3} \left[\frac{1}{2} + \frac{1}{2} \operatorname{erfc}\left(-\frac{ik}{2E}\right) \right] \right\},$$

where $\operatorname{erf}(x) = 1 \operatorname{-erfc}(x)$. We are not able to track down the article describing the derivations of this expression, so we do not know what kind of approaches they took. Numerically, their result would have little difference from ours if $k \ll E \approx 1/a$, which is valid in the long wavelength limit.

(III) Vlieger¹⁷ derived an approximate expression for the tensor **C** by splitting the sum over all points of the infinite two-dimensional lattice except the origin into a sum over \mathbf{s}_{nm} with $|\mathbf{s}_{nm}| < r_0$ ($a \ll r_0 \ll 2\pi/k$) and integrals over the rest of the lattice. The result is

$$C^{zz} = -\sum_{n,m\neq 0} |\mathbf{s}_{nm}|^{-3} + 2\pi i k a^{-2} \sin^2 \theta \sec \theta - \frac{2ik^3}{3},$$

$$C^{xx} = \frac{1}{2} \sum_{n,m\neq 0} |\mathbf{s}_{nm}|^{-3} + 2\pi i k a^{-2} \cos \theta - \frac{2ik^3}{3},$$

$$C^{yy} = \frac{1}{2} \sum_{n,m\neq 0} |\mathbf{s}_{nm}|^{-3} + 2\pi i k a^{-2} \sec \theta - \frac{2ik^3}{3},$$

(2.40)

where θ is the angle of incidence. The infinite lattice sum for a square lattice was obtained by Van der Hoff and Benson,¹⁸

$$a^{3} \sum_{n,m \neq 0} |\mathbf{s}_{nm}|^{-3} = 9.0336217.$$
A numerical check for both the real and imaginary parts, shows that the analytical expressions in Eq.(2.40) are excellent approximate results. They present good numerical agreements with our result (see Tables 2.1, 2.2 and 2.3 for |i - j| = 0), although they are limited to the case of a square lattice and small values of *k*.

In Eq.(2.39), $\operatorname{erfc}(-ik/2E)$ is almost equal to 1 because E >> k in the long wavelength limit. The imaginary term $-(2/3)ik^3$, although very small, cancels the radiation damping term in the polarizability α in Lorentz oscillator model of radiation from a bound charge.^{13,17,19} The radiation damping is a radiative interaction to describe the energy loss through radiation and the subsequent effect on the motion of the source charge while the motion produces radiation. Tensor **D** of Eq.(2.39) is added to obtain tensor **C** in Eq.(2.38) in order to subtract the contribution from the self-interaction of the electric dipole moment. Thus the cancellation of $-(2/3)ik^3$ in Eq.(2.39) is consistent with the dipole moment interacting with its own radiation field. Later in the treatment of a semi-infinite bulk, with the approximate analytical expression in Eq.(2.40), we shall show that, without the cancellation due to radiation damping in a system with a real polarizability, $-(2/3)ik^3$ will cause the solution of the self-consistent dipole moment to diverge.

2.3.3 Numerical Results

The convergent results of equations (2.34)-(2.39) and (2.29) are demonstrated in the following three Tables (2.1-2.3). The calculation was performed on a lattice with a square structure, $\xi = 0$ and $\zeta = 1$ in Eq.(2.18), of a = 2.5 Angstroms. The photon energy is 2 eV, the angle of incidence is 45 degree, and the plane of incidence is along the *x*-axis. N and P are the maximum values of |n| + |m| and |p| + |q|, respectively, for each sum, in real and reciprocal lattice spaces, to converge up to seven significant digits.

<u> i-j </u>	E = 1/a	N.P	E = 2/a	N.P	E = 5/a	N,P
0	4.51680e+0 + <i>i</i> 1.12562e	-252	4.51681e+0 + <i>i</i> 1.125	i62e-2 3 3	4.51683e+0 + <i>i</i> 1.12	2562e-2 3 7
1	-1.63753e-1 + <i>i</i> 1.12562e	-252	-1.63753e-1 + <i>i</i> 1.125	562e-2 3 3	-1.63753e-1 + i1.11	2562e-2 3 4
2	-3.17821e-4 + <i>i</i> 1.12562e	-203	-3.17821e-4 + i1.125	562e-2 3 3	-3.17821e-4 + <i>i</i> 1.12	2562e-2 3 3
3	-6.10103e-5 + <i>i</i> 1.12561e	-2 0 2	-6.10103e-5 + i1.125	561e-2 3 2	-6.10103e-5 + <i>i</i> 1.12	2561e-2 3 2
4	-8.06618e-5 + <i>i</i> 1.12559e	-2 0 2	-8.06618e-5 + <i>i</i> 1.125	59e-2 3 2	-8.06618e-5 + <i>i</i> 1.12	2559e-2 3 2
5	-1.00826e-4 + <i>i</i> 1.12558e-	-2 0 1	-1.00826e-4 + <i>i</i> 1.125	58e-2 3 1	-1.00826e-4 + i1.12	2558e-2 2 1
6	-1.20990e-4 + <i>i</i> 1.12556e-	-2 0 1	-1.20990e-4 + i1.125	56e-2 3 1	-1.20990e-4 + i1.12	2556e-2 2 1
7	-1.41154e-4 + <i>i</i> 1.12553e-	201	-1.41154e-4 + <i>i</i> 1.125	53e-2 3 1	-1.41154e-4 + <i>i</i> 1.12	2553e-2 2 1
8	-1.61317e-4 + <i>i</i> 1.12551e-	201	-1.61317e-4 + <i>i</i> 1.125	51e-2 3 1	-1.61317e-4 + <i>i</i> 1.12	2551e-2 2 1
9	-1.81480e-4 + <i>i</i> 1.12548e-	201	-1.81480e-4 + i1.125	48e-2 3 1	-1.81480e-4 + i1.12	2548e-2 2 1
10	-2.01643e-4 + i1.12544e-	201	-2.01643e-4 + i1.125	44e-2 3 1	-2.01643e-4 + i1.12	2544e-2 2 1

Table 2.1: $a^{3}(\mathbf{F}_{i})^{xx}$ of a cubic lattice with $ka \approx 2\pi/2480$ and 45° incidence.

Table 2.2: $a^{3}(\mathbf{F}_{ii})^{yy}$ of a cubic lattice with $ka \approx 2\pi/2480$ and 45° incidence.

<u> i-j </u>	E = 1/a	N,P	E = 2/a	N,P	E = 5/a	N,P
0	4.51680e+0 + <i>i</i> 2.25125e-	252	4.51681e+0 + <i>i</i> 2.2	25125e-2 3 3	4.51683e+0 + <i>i</i> 2.	25125e-2 3 7
1	-1.63773e-1 + <i>i</i> 2.25124e	-2 5 2	-1.63773e-1 + i2.2	25124e-2 3 3	-1.63773e-1 + <i>i</i> 2.	25124e-2 3 4
2	-3.58150e-4 + i2.25123e	203	-3.58150e-4 + i2.2	25123e-2 3 3	-3.58150e-4 + i2.	25123e-2 3 3
3	-1.21506e-4 + i2.25121e-	202	-1.21506e-4 + i2.2	25121e-2 3 2	-1.21506e-4 + i2.	25121e-2 3 2
4	-1.61323e-4 + <i>i</i> 2.25119e-	202	-1.61323e-4 + <i>i</i> 2.2	25119e-2 3 2	-1.61323e-4 + <i>i</i> 2.	25119e-2 3 2
5	-2.01651e-4 + <i>i</i> 2.25116e-	201	-2.01651e-4 + i2.2	25116e-2 4 1	-2.01651e-4 + i2.	25116e-2 2 1
6	-2.41980e-4 + <i>i</i> 2.25112e-	201	-2.41980e-4 + i2.2	25112e-2 3 1	-2.41980e-4 + i2.	25112e-2 2 1
7	-2.82308e-4 + i2.25107e-	201	-2.82308e-4 + i2.2	25107e-2 4 1	-2.82308e-4 + i2.	25107e-2 2 1
8	-3.22635e-4 + i2.25102e-	201	-3.22635e-4 + i2.2	5102e-2 3 1	-3.22635e-4 + i2.	25102e-2 2 1
9	-3.62961e-4 + i2.25095e-	201	-3.62961e-4 + i2.2	5095e-2 3 1	-3.62961e-4 + i2.	25095e-2 2 1
	-4.03286e-4 + i2.25089e-	201	-4.03286e-4 + i2.2	5089e-2 3 1	-4.03286e-4 + i2.1	25089e-2 2 1

<u>li-jl</u>	E = 1/a	N.P	E = 2/a	N.P	E = 5/a	N.P
0	-9.03363e0 + <i>i</i> 1.12562e-2	2.5.2	-9.03362e0 + <i>i</i> 1.12562e	-2 33	-9.03360e() + /1.12562e-2	3.6
1	3.27445e-1 + <i>i</i> 1.12562e-2	2 5 2	3.27445e-1 + <i>i</i> 1.12562e	-2 3 3	3.27445e-1 + <i>i</i> 1.12562e-2	34
2	5.14649e-4 + <i>i</i> 1.12562e-2	2 0 3	5.14649e-4 + <i>i</i> 1.12562e	-233	5.14649e-4 + <i>i</i> 1.12562e-2	33
3	-5.94668e-5 + <i>i</i> 1.12561e-3	202	-5.94668e-5 + <i>i</i> 1.125616	e-232	-5.94668e-5 + <i>i</i> 1.12561e-2	232
4	-8.06589e-5 + <i>i</i> 1.12559e-2	202	-8.06589e-5 + i1.12559e	e-232	-8.06589e-5 + <i>i</i> 1.12559e-2	232
5	-1.00826e-4 + <i>i</i> 1.12558e-2	201	-1.00826e-4 + <i>i</i> 1.125586	e-2 3 1	-1.00826e-4 + <i>i</i> 1.12558e-2	221
6	-1.20990e-4 + <i>i</i> 1.12556e-2	201	-1.20990e-4 + <i>i</i> 1.12556e	e-2 3 1	-1.20990e-4 + i1.12556e-2	221
7	-1.41154e-4 + <i>i</i> 1.12553e-2	2 0 1	-1.41154e-4 + <i>i</i> 1.12553e	e-2 3 1	-1.41154e-4 + <i>i</i> 1.12553e-2	2 2 1
8	-1.61317e-4 + <i>i</i> 1.12551e-2	2 0 1	-1.61317e-4 + i1.12551e	-231	-1.61317e-4 + <i>i</i> 1.12551e-2	2 2 1
9	-1.81480e-4 + <i>i</i> 1.12548e-2	2 0 1	-1.81480e-4 + <i>i</i> 1.12548e	-231	-1.81480e-4 + <i>i</i> 1.12548e-2	2 2 1
10	-2.01643e-4 + i1.12544e-2	201	-2.01643e-4 + i1.12544e	-231	-2.01643e-4 + i1.12544e-2	2 2 1

Table 2.3: $a^{3}(\mathbf{F}_{ii})^{zz}$ of a cubic lattice with $ka \approx 2\pi/2480$ and 45° incidence.

For $|i - j| \ge 2$, the \mathbf{F}_{ij} in the third (E = 2/a) and fourth (E = 5/a) columns are calculated from Eqs.(2.34)-(2.37), while those of the second column (E = 1/a) are calculated simply by Eq.(2.29) in which the calculation does not involve the parameter *E* and N = 0 is irrelevant. The numbers in these Tables demonstrate that the choice of the parameter *E* does not affect the calculated results but only the computational efficiency. These consistent results provide us with great confidence in both the mathematical derivation and the computer programming.

In the next Table, the third column is calculated from the contribution of p = q = 0 in Eq.(2.29) only. It can be seen clearly that the long range electric dipole field, *i.e.* the dc term of the reciprocal lattice sum, dominates the planar interaction for $|i - j| \ge 2$. But for the neighboring planes, |i - j| = 1, the short range field also contributes, and the calculation has to count on the presence of |p| + |q| up to 4 in Eq.(2.29). We shall revisit this point later in the bulk treatment of the dipole wave decomposition.

<u> i-j </u>	Complete formula	Eq.(29) with $p = q = 0$		
0	4.51493 + <i>i</i> 0.15919	0. $+i0.15919$		
1	-0.16777 + <i>i</i> 0.15914	-4.03e-3 + <i>i</i> 0.15914		
2	-8.34e-3 + <i>i</i> 0.15898	-8.06e-3 + <i>i</i> 0.15898		
3	-1.21e-2 + <i>i</i> 0.15873	-1.21e-2 + <i>i</i> 0.15873		
4	-1.61e-1 + <i>i</i> 0.15837	-1.61e-1 + <i>i</i> 0.15837		
5	-2.01e-2 + <i>i</i> 0.15791	-2.01e-2 + <i>i</i> 0.15791		

Table 2.4: $a^{3}(\mathbf{F}_{i})^{xx}$ of a cubic lattice with $ka \approx 2\pi/248$ and normal incidence.

2.4 Calculation for a Finite Number of Layers

Now, Eq.(2.21), $\sum_{j=0} [\alpha_i^{-1} \delta_{ij} - \mathbf{F}_{ij}] \cdot \mathbf{p}_j = \mathbf{E}_0 e^{i\mathbf{k}\cdot\mathbf{r}_i}$, is ready to be solved as a matrix equation. The external field on the right hand side is a composite column vector of $3\times(L+1)$ elements for a system of finite (L+1) layers. The matrix on the left hand side is also a composite square matrix of 3×3 matrices with total dimension $[3\times(L+1)]$. The matrix equation is solved by a computer program, modified for complex numerical computation, from Numerical Recipes in \mathbb{C}^{20} using the *LU* decomposition, back-substitution and an iterative improvement procedure for solutions to linear equations. *L* and *U* stand for lower and upper triangular matrices. The computation time scales as $[3\times(L+1)]^3$ for the matrix operations. For L = 100, it would take about 1.5 Mbytes of memory to store a matrix, and about 20 minutes for a 486 machine at 33 MHz to execute the program.

The induced dipole moment in Fig. 2.3 is calculated from a cubic lattice with a = 2.5 A. The external field ($|\mathbf{E}_0| = 1$) is linearly polarized along the *x*-axis at normal incidence. A rather high frequency field of 20eV is chosen in order to observe the full modulation of the dipole moment within 101 layers of thin film. The input polarizability tensor is diagonal and isotropic with $a^{-3}\alpha \approx 0.187$, which is equivalent to a refractive index of 3.4 according to the Lorentz-Lorenz relation,



Fig. 2.3 Dipole moments from a 101 finite layer calculation. n = 3.4, $ka \approx 2\pi/248$, $\theta = 0^{\circ}$.



Fig. 2.4 Radial and transverse components of the electric dipole field in the spherical coordinate system.

$$a^{-3}\alpha = \frac{3(n^2 - 1)}{4\pi(n^2 + 2)},$$
(2.41)

where *n* is the refractive index. We consider the high index case here to show the sizable wiggle^{10,21,22} at both interfaces. When the angle of incidence is not zero, the tangential components of the dipole moment exhibit the wiggle, but the normal (z) component does not. The magnitude of the normal components of dipole moments of the first few surface layers differs little from the rest.

The insensitivity of the normal component of the local field to the missing dipole moments on the other side of the surface can be illustrated by the sin θ dependency, where θ is the angle between a dipole vector and the radial vector, of the electric dipole field. For a dipole moment along the polar axis of a spherical coordinate system as in Fig. 2.4, the electric field is¹³

$$\mathbf{E}_{\rm dip} = \mathbf{e}_{\rm \theta} E_{\rm \theta} + \mathbf{e}_{\rm r} E_{\rm r}$$

$$= \mathbf{e}_{\theta} |\mathbf{p}| k^{3} [\frac{1}{(kr)^{3}} - \frac{i}{(kr)^{2}} - \frac{1}{kr}] \sin \theta e^{i(kr-\omega t)} + \mathbf{e}_{r} 2 |\mathbf{p}| k^{3} [\frac{1}{(kr)^{3}} - \frac{i}{(kr)^{2}}] \cos \theta e^{i(kr-\omega t)}.$$

The radial component, which has a $\cos\theta$ dependency, only contributes in the near zone where $kr \ll 1$. When we sum over the field from an infinite medium, a large number of dipole moments contribute from the far zone through the transverse component, especially the $-|\mathbf{p}|k^2\sin\theta/r$ term. The normal component of the surface local field thus sees more contributions from the dipole moments on the same surface plane and cares less about the missing dipole moments above the surface, while the tangential components see it in a different way.

The reflected field can be calculated by summing the long range parts of the electric dipole fields arising from all the dipoles in the medium. Define two tensors, **D** and **B**, from the expression in Eq.(2.29),

$$(\mathbf{F}_{ij})^{uv} = \frac{2\pi i}{A} \sum_{p,q} \frac{-k_{pq}^{u} k_{pq}^{v} + k^{2} \delta_{uv}}{\kappa_{pq}} \exp[i\mathbf{k}_{pq} \cdot (\mathbf{r}_{i} - \mathbf{r}_{j})],$$

$$= \sum_{p,q} (\mathbf{D}_{pq})^{uv} \exp[i\mathbf{k}_{pq} \cdot (\mathbf{r}_{i} - \mathbf{r}_{j})] \quad \text{if } z_{i} > z_{j}, \qquad (2.42)$$

$$= \sum_{p,q} (\mathbf{B}_{pq})^{uv} \exp[i\mathbf{k}_{pq} \cdot (\mathbf{r}_{i} - \mathbf{r}_{j})] \quad \text{if } z_{i} < z_{j}.$$

Then we have the reflected field (with the phase of the field chosen to be zero at $\mathbf{r} = 0$)

$$\mathbf{E}_{r} = \sum_{i=0}^{L} \mathbf{D}_{00} \cdot \mathbf{p}_{i} \exp(-i\mathbf{k}_{00} \cdot \mathbf{r}_{i}),$$

where $\mathbf{k}_{00} = (k^x, k^y, |k^z|)$. The calculated magnitude of \mathbf{E}_r is plotted against the number of layers in Fig. 2.5 with the same input parameters as in Fig. 2.3. The modulation is expected as the result of interference between the upper and lower surface reflections with varying thin film thickness. In real situations, we usually do not see the interference from a macroscopic object with a beam of finite size. But in our treatment of a finite number layers, the interference is inevitable even with non zero angle of incidence because we only handle the infinite plane wave. The goal of eliminating this interference because of a semi-infinite bulk medium.

2.5 Dipolar Interaction of the Surface and the Bulk

The semi-infinite system is separated into a surface region consisting of a finite number of layers and a bulk region with the same lattice structure and unit cell polarizability tensor α_b . The planar index of surface region is i = 0, ..., L, and that of bulk region is $m = 0, 1, ..., \infty$ (Fig. 2.1). The z-component of the position vector for a lattice plane in the bulk region is $z_m = z_L - (m+1)a$. The basic equation to solve for an induced dipole moment in the surface region is



,

Fig. 2.5 The magnitude of reflected field vs the number of layers in the calculation. n = 3.4, $ka \approx 2\pi/248$, $\theta = 0^{\circ}$.

$$\sum_{j=0}^{L} [\boldsymbol{\alpha}_{i}^{-1} \boldsymbol{\delta}_{ij} - \mathbf{F}_{ij}] \cdot \mathbf{p}_{j} = \mathbf{E}_{0} e^{i\mathbf{k}\cdot\mathbf{r}_{i}} + \mathbf{E}_{dip}^{bulk} (\mathbf{r}_{i}) = \mathbf{E}_{0} e^{i\mathbf{k}\cdot\mathbf{r}_{i}} + \sum_{m=0}^{\infty} \mathbf{F}_{im} \cdot \mathbf{p}_{m}.$$
 (2.43)

The basic equation to solve for an induced dipole moment in the bulk region is

$$\sum_{j=0}^{\infty} [\boldsymbol{\alpha}_{\mathrm{b}}^{-1} \boldsymbol{\delta}_{mj} - \mathbf{F}_{mj}] \cdot \mathbf{p}_{j} = \mathbf{E}_{0} e^{i\mathbf{k}\cdot\mathbf{r}_{m}} + \mathbf{E}_{\mathrm{dip}}^{\mathrm{surf}}(\mathbf{r}_{m}) = \mathbf{E}_{0} e^{i\mathbf{k}\cdot\mathbf{r}_{m}} + \sum_{i=0}^{L} \mathbf{F}_{mi} \cdot \mathbf{p}_{i}. \quad (2.44)$$

The left hand side of Eq.(2.44) can be rewritten as

$$\sum_{j=0}^{\infty} [\boldsymbol{\alpha}_{b}^{-1} \boldsymbol{\delta}_{mj} - \mathbf{F}_{mj}] \cdot \mathbf{p}_{j} = \sum_{j=0}^{\infty} [(\boldsymbol{\alpha}_{b}^{-1} - \mathbf{C}) \boldsymbol{\delta}_{mj} - \mathbf{F}_{m \neq j}] \cdot \mathbf{p}_{j}$$

Eq.(2.42) has introduced two tensors (**D** and **B**) for the interplanar dipolar interaction, and we repeat it here for the proper bulk layer index:

$$(\mathbf{F}_{m\neq j})^{\mu\nu} = \frac{2\pi i}{A} \sum_{p,q} \frac{-k_{pq}^{\mu} k_{pq}^{\nu} + k^{2} \delta_{\mu\nu}}{\kappa_{pq}} \exp[ik_{pq}^{z} (z_{m} - z_{j})],$$

$$= \sum_{p,q} (\mathbf{D}_{pq})^{\mu\nu} \exp[i\kappa_{pq} (z_{m} - z_{j})] \quad \text{if } z_{m} > z_{j}, \qquad (2.45)$$

$$= \sum_{p,q} (\mathbf{B}_{pq})^{\mu\nu} \exp[-i\kappa_{pq} (z_{m} - z_{j})] \quad \text{if } z_{m} < z_{j},$$

where we have taken the origin of each planar lattice $\mathbf{r}_m^* = 0$, as it should be for a single system, so that $\mathbf{r}_m = \mathbf{z} \mathbf{z}_m = \mathbf{z} [z_L - (m+1)a]$. The definitions of Eq.(2.45) provide us with

$$\sum_{j=0}^{\infty} \mathbf{F}_{m\neq j} \cdot \mathbf{p}_{j} = \sum_{p,q} \left\{ \left[\mathbf{B}_{pq} \cdot \sum_{j=0}^{m-1} \mathbf{p}_{j} e^{i\kappa_{pq}(m-j)a} \right] + \left[\mathbf{D}_{pq} \cdot \sum_{j=m+1}^{\infty} \mathbf{p}_{j} e^{i\kappa_{pq}(j-m)a} \right] \right\}.$$
 (2.46)

2.6 Dipole Wave Decomposition

It has been suggested that the field response from a bulk medium can be decomposed into an infinite number of modes of dipole waves in the medium.⁶ The dipole moment of lattice plane m is expressed as

$$\mathbf{p}_m = \sum_{h=0}^{\infty} v_h \mathbf{u}_h \exp(-i\psi_h ma), \qquad (2.47)$$

where ψ_h is the z-component of the wave vector of dipole wave mode h, \mathbf{u}_h is the polarization vector and v_h the magnitude. Substituting Eq.(2.47) into Eq.(2.46) yields

$$\sum_{j=0}^{\infty} \mathbf{F}_{m \neq j} \cdot \mathbf{p}_{j} = \sum_{h=0}^{\infty} v_{h} \sum_{p,q} \left\{ \left[\mathbf{B}_{pq} \cdot \mathbf{u}_{h} \sum_{j=0}^{m-1} e^{-i\psi_{h}ja} e^{i\kappa_{pq}(m-j)a} \right] + \left[\mathbf{D}_{pq} \cdot \mathbf{u}_{h} \sum_{j=m+1}^{\infty} e^{-i\psi_{h}ja} e^{i\kappa_{pq}(j-m)a} \right] \right\}.$$
(2.48)

To evaluate the summation series in the brackets of the last equation, we use the following identities:

$$\sum_{t=0}^{n} x^{t} = \frac{1 - x^{n+1}}{1 - x},$$
(2.49)

and

$$\sum_{t=1}^{\infty} x^{t} = \frac{1}{1-x} - 1 = \frac{x}{1-x}.$$
(2.50)

In Eq.(2.50), x < 1 is required so that the infinite series converges.

With the identity of Eq.(2.49), the first series in the right hand side of Eq.(2.48) becomes

$$\sum_{j=0}^{m-1} e^{-i\psi_h j a} e^{i\kappa_{pq}(m-j)a} = e^{i\kappa_{pq}ma} \sum_{j=0}^{m-1} e^{-i(\kappa_{pq}+\psi_h)ja} = e^{i\kappa_{pq}ma} \frac{1-e^{-i(\kappa_{pq}+\psi_h)ma}}{1-e^{-i(\kappa_{pq}+\psi_h)a}},$$
$$= \frac{e^{-i\psi_h ma} - e^{i\kappa_{pq}ma}}{e^{-i(\kappa_{pq}+\psi_h)a} - 1}.$$
(2.51)

Also, the second series in Eq.(2.48), with the help of Eq.(2.50), becomes

$$\sum_{j=m+1}^{\infty} e^{-i\psi_{h}ja} e^{i\kappa_{pq}(j-m)a} = e^{-i\psi_{h}ma} \sum_{j=m+1}^{\infty} e^{i(\kappa_{pq}-\psi_{h})(j-m)a} = e^{-i\psi_{h}ma} \sum_{j'=1}^{\infty} e^{i(\kappa_{pq}-\psi_{h})j'a},$$
$$= e^{-i\psi_{h}ma} \frac{e^{i(\kappa_{pq}-\psi_{h})a}}{1-e^{i(\kappa_{pq}-\psi_{h})a}} = \frac{e^{-i\psi_{h}ma}}{e^{-i(\kappa_{pq}-\psi_{h})a}-1}.$$
(2.52)

When applying the series identity to obtain the last result, we have assumed that $e^{i(\kappa_{pq}-\psi_h)a} < 1$. This condition can hold only if $\text{Im}(\kappa_{pq}-\psi_h) \ge 0$. Since $\kappa_{00} = |k^z| = -k^z$ or $\kappa_{pq} = i |\kappa_{pq}|$ by definition, we only need ψ_h to have a zero or negative imaginary part. This conclusion is consistent with the expression in Eq.(2.47), where the positive imaginary part of ψ_h will cause the dipole moment \mathbf{p}_m to blow up as $m \to \infty$.

Substituting the results of Eq.(2.51) and Eq.(2.52) into Eq.(2.48), Eq.(2.44) then becomes

$$\begin{aligned} \ln s &= \sum_{j=0}^{\infty} \left[(\alpha_{b}^{-1} - \mathbf{C}) \delta_{nj} - \mathbf{F}_{m \neq j} \right] \cdot \mathbf{p}_{j} = (\alpha_{b}^{-1} - \mathbf{C}) \cdot \left(\sum_{h=0}^{\infty} v_{h} \mathbf{u}_{h} e^{-i\psi_{h}ma} \right) \\ &- \sum_{h=0}^{\infty} v_{h} \sum_{p,q} \left[\mathbf{D}_{pq} \cdot \mathbf{u}_{h} \frac{e^{-i\psi_{h}ma}}{e^{-i(\kappa_{pq} - \psi_{h})a} - 1} + \mathbf{B}_{pq} \cdot \mathbf{u}_{h} \frac{e^{-i\psi_{h}ma} - e^{i\kappa_{pq}ma}}{e^{-i(\kappa_{pq} + \psi_{h})a} - 1} \right] \\ &= \sum_{h=0}^{\infty} v_{h} \left\{ (\alpha_{b}^{-1} - \mathbf{C}) - \sum_{p,q} \left[\frac{\mathbf{D}_{pq}}{e^{-i(\kappa_{pq} - \psi_{h})a} - 1} + \frac{\mathbf{B}_{pq}}{e^{-i(\kappa_{pq} + \psi_{h})a} - 1} \right] \right\} \cdot \mathbf{u}_{h} e^{-i\psi_{h}ma} \\ &+ \sum_{h=0}^{\infty} v_{h} \sum_{p,q} \frac{\mathbf{B}_{pq} \cdot \mathbf{u}_{h}}{e^{-i(\kappa_{pq} + \psi_{h})a} - 1} e^{i\kappa_{pq}ma}, \end{aligned}$$
(2.53)

while $\operatorname{rhs} = \mathbf{E}_{0} e^{i\mathbf{k}\cdot\mathbf{r}_{m}} + \sum_{i=0}^{L} \mathbf{F}_{mi} \cdot \mathbf{p}_{i} = \mathbf{E}_{0} e^{i\kappa_{00}(ma+a-z_{L})} + \sum_{i=0}^{L} \sum_{p,q} \mathbf{B}_{pq} e^{i\kappa_{pq}(ma+a-z_{L}+z_{j})} \cdot \mathbf{p}_{i}.$ (2.54)

The last expression in Eq.(2.54) is the direct result of the definition in Eq.(2.45) that the bulk region lies underneath the surface region in our geometry. There are two wave components in Eq.(2.53), one represented by wave vector *z*-component ψ_h and the other by κ_{pq} . But the electric field in Eq.(2.54) is only represented by wave vector component κ_{pq} . For Eq.(2.44) to be true for any arbitrary dipole wave mode *h* in Eqs.(2.53) and (2.54), it requires

$$\left\{ (\boldsymbol{\alpha}_{b}^{-1} - \mathbf{C}) - \sum_{p,q} \left[\frac{\mathbf{D}_{pq}}{e^{-i(\kappa_{pq} - \Psi_{b})a} - 1} + \frac{\mathbf{B}_{pq}}{e^{-i(\kappa_{pq} + \Psi_{b})a} - 1} \right] \right\} \cdot \mathbf{u}_{h} = 0, \quad (2.55)$$

and

$$\sum_{h=0}^{\infty} v_h \sum_{p,q} \frac{\mathbf{B}_{pq} \cdot \mathbf{u}_h}{e^{-i(\kappa_{pq} + \psi_h)a} - 1} e^{i\kappa_{pq}ma} = \mathbf{E}_0 e^{i\kappa_{00}(ma + a - z_L)} + \sum_{i=0}^L \sum_{p,q} \mathbf{B}_{pq} e^{i\kappa_{pq}(ma + a - z_L + z_j)} \cdot \mathbf{p}_i .$$
(2.56)

For each pair (p,q), there is a 3-D vector equation according to Eq.(2.56). But one equation requires special attention, that being the contribution of the (0,0) term,

$$\sum_{h=0}^{\infty} v_{h} \frac{\mathbf{B}_{00} \cdot \mathbf{u}_{h}}{e^{-i(\kappa_{pq} + \Psi_{h})a} - 1} e^{i\kappa_{00}ma} - \sum_{i=0}^{L} \mathbf{B}_{00} e^{i\kappa_{00}(ma + a - z_{L} + z_{j})} \cdot \mathbf{p}_{i} = \mathbf{E}_{0} e^{i\kappa_{00}(ma + a - z_{L})},$$
$$\sum_{h=0}^{\infty} v_{h} \frac{\mathbf{B}_{00} \cdot \mathbf{u}_{h}}{e^{-i(\kappa_{pq} + \Psi_{h})a} - 1} e^{-i\kappa_{00}(a - z_{L})} - \sum_{i=0}^{L} \mathbf{B}_{00} e^{i\kappa_{00}z_{j}} \cdot \mathbf{p}_{i} = \mathbf{E}_{0}.$$
(2.57)

The physical interpretation of Eq.(2.57) is analogous to the Ewald-Oseen extinction theorem.^{14,19,23} The external field $E_0 e^{i\mathbf{k}\cdot\mathbf{r}}$ is cancelled at every point within the medium due to interference with the emitted electric dipole field and replaced by the field propagating with the correct phase velocity. The theorem was derived for the continuous medium in the form of integral equations in the Lorentz gauge by Born and Wolf.¹⁴ Sipe and van Kranendonk²³ also obtained the microscopic extinction theorem with the discrete lattice model, but the electric dipole field was treated in the Coulomb gauge, that is with instantaneous rather than retarded fields.

2.6.1 The Solutions

or

Eq.(2.55) can hold for nontrivial solutions for \mathbf{u}_h only if the 3×3 matrix is singular. That is the determinant of that matrix has to be zero,

$$\det \mathbf{A} = \det \left\{ (\boldsymbol{\alpha}_{b}^{-1} - \mathbf{C}) - \sum_{p,q} \left[\frac{\mathbf{D}_{pq}}{e^{-i(\kappa_{pq} - \psi_{b})a} - 1} + \frac{\mathbf{B}_{pq}}{e^{-i(\kappa_{pq} + \psi_{b})a} - 1} \right] \right\} = 0. \quad (2.58)$$

Since det $\mathbf{D}_{pq} = \det \mathbf{B}_{pq}$ from the definition in Eq.(2.45), det **A** is an even function of ψ_h . The positive real part of ψ_h describes the dipole wave propagating upward in the medium, and the negative one the downward propagating wave. For a semi-infinite medium in the lower space, the downward propagation is wanted because there is no lower boundary to reflect the waves upward. These downward propagating dipole waves give rise to the reflected field into the upper space off the vacuum/medium interface. In the case of a finite number of layers, the treatment, which we have presented in the previous section, includes implicitly both the upward and downward propagating dipole waves in the self-consistent calculation. The result is an interference modulation in the reflected field as the number of layers increases, as shown in Fig. 2.5. Therefore, the discussions of ψ_h from here on in our semi-infinite model will only refer to ψ_h with negative values.

The number of roots of Eq.(2.58) depends on the number of terms of (p,q). Generally, each (p,q) term is associated with two roots, but, in the case of normal incidence the two become degenerate. In the long wavelength limit, only two ψ_{μ} , associated with $-\kappa_{00} = k^2$, have nonzero real parts (Fig. 2.6), and they represent the propagating components of these decomposed dipole waves in the medium. We label these two dipole wave modes as h = 0 and 1. The other modes, due to the pure imaginary nature of ψ_h , represent the evanescent waves and they are exponentially damped. The evanescent modes are important to evaluate the exact dipole moments near the bulk boundary (small m). But the real material boundary is in the surface region (*i.e.* i = 0 for a single medium). This bulk boundary (m = 0) is just an artifact in our treatment. The two propagating modes of dipole waves are sufficient to represent the bulk dipole contribution to the surface local field, as long as the choice of the number of surface layers, L+1, is large enough to match the bulk dipoles in the lower surface region. According to the numerical results that we will present later (section 2.8), L = 5is a good enough choice for the usual low to moderate polarizability medium, while the extremely polarizable medium requires no more than 10 layers.

Although we have concluded that we only need to find roots ψ_0 and ψ_1 from Eq.(2.58), the matrix elements of **A** still have to be the convergent results of the reciprocal lattice sum. This is because the near field arising from terms $(p,q) \neq (0,0)$ also contributes to the propagating dipole waves. Table 2.5 shows the varying real part of ψ_0



Fig. 2.6 DetA of Eq.(2.58) vs real part of ψ_h . There are two roots of detA = 0 with nonzero real part of ψ_h . n = 3.4, $ka \approx 2\pi/2480$, $\theta = 45^\circ$.

and ψ_1 with P being the maximum |p| + |q| used in the reciprocal lattice sum.

 $\psi_f = -nk\sqrt{1 - \left(\frac{\sin\theta}{n}\right)^2}$ is the corresponding wave vector from the continuum

approach, the result of Snell's law.

=

(the real part) with the near field contributions included in Eq.(2.58).							
	$(n=4.0/\theta=30^{\circ}/ka=0.025)$		(<i>n</i> =4.0/θ=30°	<i>p/ka=</i> 0.0025)	(1.5/0º/0.0025)		
P	-ψ ₀	-ψ1	-ψ ₀	-Ψ ₁	$-\mathbf{\Psi}_0 = -\mathbf{\Psi}_1$		
0	0.1264182	0.1275498	0.01266025	0.01276917	0.003835753		
1	0.1023665	0.1024883	0.01023767	0.01024658	0.003803743		
2	0.1005734	0.1006069	0.01005780	0.01005799	0.003800373		
3	0.1005428	0.1005748	0.01005474	0.01005478	0.003800314		
	0.1005422	0.1005742	0.01005468	0.01005471	0.003800313		
<u>-Ψ</u>	0.1005468		0.01005468		0.003800314		

Table 2.5: Convergent numerical results of wave vectors ψ_0 and ψ_1 (the real part) with the near field contributions included in Eq.(2.58)

The values of ψ_0 and ψ_1 do not change for P beyond 4. If we take the bulk results from calculations with P = 0 or 1, the equivalent refractive index of the bulk will be different from that of the surface region and we will still have interference due to the extra reflection at the surface/bulk boundary.

2.7 Divergent Dipole Moment and Self-interaction

The discussion after Eq.(2.52) leads to the conclusion that Ψ_h must have a zero or negative imaginary part in order to prevent divergent dipole moments in the semiinfinite medium. This conclusion also presents an argument for keeping the $(2/3)ik^3$ selfinteraction term in the lattice summation problem. For simplicity we consider the case of an external field, with s-polarization, linearly polarized along the y-axis. We also ignore the contribution from terms of $(p,q) \neq (0,0)$ in the evaluation of elements of

matrix **A**. We have
$$\mathbf{B}_{00} = \begin{bmatrix} b^{xx}, 0, b^{xz} \\ 0, b^{yy}, 0 \\ b^{zx}, 0, b^{zz} \end{bmatrix}$$
 and $\mathbf{D}_{00} = \begin{bmatrix} d^{xx}, 0, d^{zz} \\ 0, d^{yy}, 0 \\ d^{zx}, 0, d^{zz} \end{bmatrix}$ because $k^{y} = 0$.

For an isotropic medium with a cubic lattice, both α_{b} and C are diagonal. The polarization vector **u** of one dipole wave mode is (0,1,0). Eq.(2.55) reduces to

$$(\alpha_{b}^{-1} - c^{yy}) - \frac{d^{yy}}{e^{-i(\kappa_{00} - \psi)a} - 1} - \frac{b^{yy}}{e^{-i(\kappa_{00} + \psi)a} - 1} = 0$$

According to Eq.(2.45), we have $b^{yy} = d^{yy} = 2\pi i a^{-2} k^2 / |k^2| = 2\pi i a^{-2} k / \cos\theta$. The last

equation becomes $(\alpha_{b}^{-i} - c^{yy}) - \frac{b^{yy}(e^{-i(\kappa_{00} - \psi)a} + e^{-i(\kappa_{00} + \psi)a} - 2)}{(e^{-i(\kappa_{00} - \psi)a} - 1)(e^{-i(\kappa_{00} + \psi)a} - 1)}$

$$= \alpha_{\rm b}^{-1} - c^{yy} - \frac{b^{yy} e^{-i\kappa_{00}a} \left(2\cos a\psi - 2e^{i\kappa_{00}a}\right)}{e^{-2i\kappa_{00}a} - e^{-i\kappa_{00}a} \left(2\cos a\psi\right) + 1} = 0$$

After some rearrangements of the last eqution, we have

$$(\alpha_{b}^{-1} - c^{yy})(\cos a\kappa_{00} - \cos a\psi) = b^{yy}(\cos a\psi - \cos a\kappa_{00} - i\sin a\kappa_{00}),$$
$$(\alpha_{b}^{-1} - c^{yy} + b^{yy})(\cos a\psi - \cos a\kappa_{00}) = ib^{yy}\sin a\kappa_{00},$$

and

d
$$\cos a\psi = \cos a\kappa_{00} + \frac{ib^{yy}\sin a\kappa_{00}}{\alpha_{b}^{-1} - c^{yy} + b^{yy}} \approx \cos a\kappa_{00} - \frac{2\pi a^{-1}k^{2}}{\alpha_{b}^{-1} - c^{yy} + b^{yy}}$$

We bring in here the analytical expression for c^{yy} by Vlieger¹⁷ as in Eq.(2.40):

$$c^{yy} = \frac{1}{2} \sum_{n,m \neq 0} |\mathbf{s}_{nm}|^{-3} + 2\pi i k a^{-2} \sec \theta - \frac{2ik^3}{3} = \Delta + b^{yy} - \frac{2ik^3}{3}$$

where $\Delta = \frac{1}{2} \sum_{n,m \neq 0} |\mathbf{s}_{nm}|^{-3}$ is real. Our expression for ψ becomes

$$\cos a\psi = \cos a\kappa_{00} - \frac{2\pi a^{-1}k^2}{(\alpha_{\rm b}^{-1} - \Delta) + 2ik^3/3}.$$
 (2.59)

If α_{b} in Eq.(2.59) is real, *i.e.* not a damping term, we then have

$$\cos a \Psi = \cos a \kappa_{00} - \frac{2\pi a^{-1} k^2 (\alpha_b^{-1} - \Delta - 2ik^3 / 3)}{(\alpha_b^{-1} - \Delta)^2 + (2k^3 / 3)^2}.$$
 (2.60)

The imaginary part of the last term is positive. For an arbitrary complex number z = u + iv,

$$\cos z = \cos(u + iv) = \frac{1}{2} (e^{iu} e^{-v} + e^{-iu} e^{v}) = \frac{1}{2} [\cos u (e^{-v} + e^{v}) + i \sin u (e^{-v} - e^{v})].$$

The last expression shows that $\cos(z)$ can have a positive imaginary part only if *u* and *v* have opposite sign ($u \cdot v < 0$). The presence of $2ik^3/3$ in Eq.(2.60) assures that we will obtain ψ with a negative real part and a positive imaginary part. In order to prevent divergent dipole moments, $2ik^3/3$ has to be eliminated either by including a self-field in the lattice summation for tensor **C** or by including the radiation damping in α . The equivalence of these two approaches can be justified by a classical harmonic oscillator model.¹⁹

2.7.1 Self-interaction and Radiation Damping

Consider a particle of mass *m* and charge *q* bound by a spherically symmetric, linear, restoring force $m\omega_0^2 \mathbf{r}$, in the presence of a given external field $\mathbf{E}e^{i\omega r}$. The equation of motion is: $m(\ddot{\mathbf{r}} + \omega_0^2 \mathbf{r} - \tau \ddot{\mathbf{r}}) = q\mathbf{E}e^{i\omega r}$, (2.61) where $\tau = (2q^2/3mc^3)$ is the radiation damping constant.¹³ The steady-state solution is

$$\mathbf{r} = \frac{q}{m} \frac{\mathbf{E}e^{i\omega t}}{\omega_0^2 - \omega^2 - i\omega^3 \tau}$$

The induced dipole moment is obtained by $\mathbf{p} = q\mathbf{r} = \alpha \mathbf{E}e^{i\omega t}$, and the complex

polarizability is
$$\alpha = \frac{q^2}{m} \frac{1}{\omega_0^2 - \omega^2 - i\omega^3 \tau} = \frac{3c^3 \tau/2}{\omega_0^2 - \omega^2 - i\omega^3 \tau}.$$
 (2.62)

Eq.(2.61) can be written in a form which includes a contribution from the self-field instead of the radiation damping, $m(\ddot{\mathbf{r}} + \omega_0^2 \mathbf{r}) = q(\mathbf{E}_{sf} + \mathbf{E})e^{i\omega t}$. (2.63)

The solution becomes $\mathbf{r} = \frac{q}{m} \frac{(\mathbf{E}_{sf} + \mathbf{E})e^{i\omega t}}{\omega_0^2 - \omega^2}$, and the real polarizability according to

Eq.(2.63) is
$$\alpha_0 = \frac{q^2}{m} \frac{1}{\omega_0^2 - \omega^2} = \frac{3c^3 \tau/2}{\omega_0^2 - \omega^2}.$$
 (2.64)

By comparing Eq.(2.62) and Eq.(2.64), it is obvious that

$$\alpha^{-1} = \alpha_0^{-1} - 2i\omega^3 / 3c^3 = \alpha_0^{-1} - 2ik^3 / 3.$$
 (2.65)

When this complex polarizability is introduced to Eq.(2.59), the cancellation of $2ik^3/3$ guarantees us to have a non-positive imaginary solution for ψ . The result of this analysis is proved to be quite general by the numerical solutions to Eq.(2.58). When $2ik^3/3$ was kept in the tensor **C**, the numerical solutions of ψ_0 and ψ_1 contained a positive imaginary part on the order of 10^{-11} . When $2ik^3/3$ was removed from the tensor **C**, the imaginary part became negative and had a value of about the machine error $(10^{-17} \text{ to } 10^{-21} \text{ in double precision})$ in a non-absorptive bulk medium.

2.8 Self-consistent Dipole Moments and Local Fields

In Eq.(2.43), the bulk contribution to the electric dipole field at the surface region can be expressed as

$$\mathbf{E}_{dip}^{bulk}(\mathbf{r}_{i}) = \sum_{m=0}^{\infty} \mathbf{F}_{im} \cdot \mathbf{p}_{m} \approx \sum_{h=0}^{1} v_{h} \sum_{p,q} \mathbf{D}_{pq} \cdot \mathbf{u}_{h} \sum_{m=0}^{\infty} e^{-i\psi_{h}ma} e^{i\kappa_{pq}(z_{i}-z_{m})},$$
$$= \sum_{h=0}^{1} v_{h} \sum_{p,q} \mathbf{D}_{pq} \cdot \mathbf{u}_{h} e^{i\kappa_{pq}(z_{i}-z_{L}+a)} \sum_{m=0}^{\infty} e^{-i\psi_{h}ma} e^{i\kappa_{pq}ma},$$

$$=\sum_{h=0}^{1} v_h \sum_{p,q} \mathbf{D}_{pq} \cdot \mathbf{u}_h \frac{e^{i\kappa_{pq}(z_i-z_L+a)}}{1-e^{i(\kappa_{pq}-\psi_h)a}}.$$
(2.66)

The series identity in Eq.(2.50) has been used to obtain this equation, and the convergent condition for that series is the same as the discussion after Eq.(2.52). Eq.(2.43) becomes

$$\sum_{j=0}^{L} \left[\boldsymbol{\alpha}_{i}^{-1} \boldsymbol{\delta}_{ij} - \mathbf{F}_{ij} \right] \cdot \mathbf{p}_{j} - \sum_{h=0}^{1} v_{h} \sum_{p,q} \mathbf{D}_{pq} \cdot \mathbf{u}_{h} \frac{e^{i\kappa_{pq}(z_{i}-z_{L}+a)}}{1 - e^{i(\kappa_{pq}-\psi_{h})a}} = \mathbf{E}_{0} e^{i\mathbf{k}\cdot\mathbf{r}_{i}}.$$
(2.67a)

This is a set of $3\times(L+1)$ linear equations for $3\times(L+1)+2$ unknowns of \mathbf{p}_i plus v_0 and v_1 . Two additional equations are obtained from Eq.(2.57), which originated from Eq.(2.44):

$$-\sum_{i=0}^{L} \mathbf{u}_{0} \cdot \mathbf{B}_{00} e^{i\kappa_{00}z_{j}} \cdot \mathbf{p}_{i} + \sum_{h=0}^{1} v_{h} \frac{\mathbf{u}_{0} \cdot \mathbf{B}_{00} \cdot \mathbf{u}_{h}}{e^{-i(\kappa_{pq} + \psi_{h})a} - 1} e^{-i\kappa_{00}(a - z_{L})} = \mathbf{u}_{0} \cdot \mathbf{E}_{0}, \quad (2.67b)$$
$$-\sum_{i=0}^{L} \mathbf{u}_{1} \cdot \mathbf{B}_{00} e^{i\kappa_{00}z_{j}} \cdot \mathbf{p}_{i} + \sum_{h=0}^{1} v_{h} \frac{\mathbf{u}_{1} \cdot \mathbf{B}_{00} \cdot \mathbf{u}_{h}}{e^{-i(\kappa_{pq} + \psi_{h})a} - 1} e^{-i\kappa_{00}(a - z_{L})} = \mathbf{u}_{1} \cdot \mathbf{E}_{0}. \quad (2.67c)$$

In Eq.(2.56), we have

$$-\sum_{i=0}^{L} \mathbf{B}_{pq} e^{i\kappa_{pq}(a-z_{L}+z_{j})} \cdot \mathbf{p}_{i} + \sum_{h=0}^{\infty} v_{h} \frac{\mathbf{B}_{pq} \cdot \mathbf{u}_{h}}{e^{-i(\kappa_{pq}+\psi_{h})a}-1} = 0$$

for each pair of $(p,q) \neq (0,0)$. These equations can be included in Eqs.(2.67) if we have to determine v_h for h > 1 (e.g. $ka \approx 1$, the short wavelength case).

Eqs.(2.67) are solved numerically using the same method used for the finite thin film case, except that the size of the matrix is expanded to $[3\times(L+1)+2]\times[3\times(L+1)+2]$. Once the induced dipole moments are determined by the matrix equations, the microscopic local field of each surface lattice site is obtained by multiplying the inverse tensor of the polarizability with the resultant dipole moment, according to the first relation in Eq.(2.1). We calculate the uniform, cubic, isotropic case so that the results can be compared to the Lorentz local field. The lattice structure and unit cell polarizability in the surface region are all taken to be identical to the bulk parameters. The lattice constant *a* is 2.5 Angstroms. The linearly polarized incident field is $|\mathbf{E}_o| = 1$ for either s- or p-polarization. To see the modulation of the local electric field at each lattice site for the discrete point dipole model, we use 101 surface layers and 20 eV for the photon energy. Although the energy is quite high, it is still within the long wavelength limit, $ka \approx 0.025$. It is chosen so that 100 layers are on the order of one wavelength of the field in the medium. For the very polarizable medium, *i.e.* very high index of refraction, the tangential components of the local field of the first couple of layers behave quite differently from the rest of the surface layers (Fig. 2.7(a)). The normal component exhibits a smaller surface anomaly (Fig. 2.7(b)). For more moderate cases of polarizability, only the topmost surface layer has a local field different from the others in an isotropic, uniform medium. The wiggles in the end of surface region, that is at the last discrete layer as seen in Fig. 2.3, disappear when we include the correct bulk contributions, the propagating dipole wave modes, from both the long and short range dipolar interactions. The depth of the surface anomaly in Fig. 2.7(a) confirms that $5 \le L \le 10$ are good choices for the number of surface layers for efficient computation.

The magnitude of the local electric field $\mathbf{E}_{loc}(\mathbf{r}_i)$ for i > 5 from our calculation is identical to the Lorentz local field for the isotropic, cubic lattice.

Lorentz local field =
$$\frac{n^2 + 2}{3} \mathbf{E}_t = \frac{n^2 + 2}{3} \frac{\cos \theta - n \cos \theta_t}{\cos \theta + n \cos \theta_t} \mathbf{E}_0$$
 for s-polarization,
= $\frac{n^2 + 2}{3} \frac{n \cos \theta - \cos \theta_t}{n \cos \theta + \cos \theta_t} \mathbf{E}_0$ for p-polarization.

The transmitted field is obtained from Fresnel formulas and θ_t is the angle of the refracted ray. Deviations from Lorentz local fields of the first surface layer in our calculations, with a photon energy of 2 eV, are presented in Fig. 2.8, *versus* refractive index, and in Fig. 2.9, *versus* angle of incidence.



(a)



Fig. 2.7 Variation in the surface local field from the semi-infinite model. The incident field is p-polarized. n = 4.0, $ka \approx 2\pi/248$, $\theta = 45^{\circ}$. (a) the tangential component. (b) the normal component.



Fig. 2.8 The local field at the surface compared to the Lorentz bulk field $(\theta = 45^{\circ})$. $ka \approx 2\pi/2480$ in the calculation.



Fig. 2.9 The local field at the surface compared to the Lorentz bulk field (n = 2.5). $ka \approx 2\pi/2480$ in the calculation.

The reflected field is just the summation of the long range electric dipole field contributions (evaluated at $\mathbf{r} = 0$), which propagates into the upper space. By using Eq.(2.66), it is

$$\mathbf{E}_{\mathbf{r}} = \sum_{i=0}^{L} \mathbf{D}_{00} \cdot \mathbf{p}_{i} \exp(-i\mathbf{k}_{00} \cdot \mathbf{r}_{i}) + \sum_{h=0}^{1} v_{h} \mathbf{D}_{00} \cdot \mathbf{u}_{h} \frac{e^{i\mathbf{\kappa}_{00}(-z_{L}+a)}}{1 - e^{i(\mathbf{\kappa}_{00} - \boldsymbol{\psi}_{h})a}},$$

where $\mathbf{k}_{00} = (k^x, k^y, |k^z|)$. This result is numerically identical to the Fresnel formula for reflection up to 6 digits for index n = 1.5 (Fig. 2.10(a)), and 5 digits for n = 4 except in the vicinity of the Brewster angle (Fig. 2.10(b)). The big spike in Fig. 2.10(b) occurs at the Brewster angle of a very polarizable medium. Calculations with a finer angular stepsize show that the reflectivity in the microscopic treatment does not approach zero while the macroscopic result does (Fig. 2.11). An explanation of this phenomenon can be extracted from the results in Fig. 2.7 through Fig. 2.9. The zero reflectivity at the Brewster angle is generally explained by the fact that the induced dipole moments oriented in the direction of propagation of the reflected field can not radiate in that direction due to $\sin\theta$ dependency of the transverse dipole field (see discussions in section 2.4). In the microscopic calculation, because the tangential component of the surface dipole has a more profound variation from the bulk dipole than the normal component does, the surface dipole has a different orientation than the bulk dipole. This allows the surface dipole to contribute to the reflected field at the bulk Brewster angle while the bulk dipole can not. Also the number of layers to display the surface effects does not depend on the wavelength, but only on the polarizability (compare Fig. 2.7 and Fig. 2.12). So the ratio of the number of surface dipole moments to the number of bulk dipole moments (characterized by the wavelength) is greater in the short wavelength case. This results in a higher reflectivity from a shorter wavelength calculation at the Brewster angle in Fig. 2.11.

.,



(b)

Fig. 2.10 The reflected field of the microscopic calculation compared to the macroscopic Fresnel result. $ka \approx 2\pi/2480$ in the calculation. The differences of the two results are less than 2.1×10^{-7} for n = 1.5 (a), and less than 3.4×10^{-6} for n = 4.0 except in the vicinity of the Brewster angle (b).



Fig. 2.11 The reflected field at the Brewster angle for an index 4.0 medium. The stepsize in the calculation is 0.01° .



Fig. 2.12 The surface local field of a long wavelength calculation. Only the real parts are plotted. The incident field is p-polarized. n = 4.0, $ka \approx 2\pi/2480$, $\theta = 45^{\circ}$.

2.9 Conclusion

The microscopic calculation of the optical response of a semi-infinite medium in the discrete point dipole model has reproduced the macroscopic results of the bulk local field and the reflected field. Yet the microscopic calculation also provides the surface local field which is important to the study of surface phenomena. The formalism we develop here is applicable to cases beyond the macroscopic, cubic, and isotropic model. The polarizability tensor (α_i), the planar lattice structure ($a, \xi, \zeta, \mathbf{r}^{\mathbf{i}}$) and the surface layer spacing (z_i) can all vary layer by layer to treat any particular surface system. The polarizability tensor can also contain complex elements to treat the absorptive medium.

In the treatment of the bulk contribution, we have stressed that the near field has to be included properly in the solutions of the propagating dipole waves even in the long wavelength limit. The energy loss due to dipole radiation (radiation damping), although it is a very small factor, has to be taken into account to prevent the dipole moment in the semi-infinite bulk from diverging.

CHAPTER III

THEORY OF SURFACE SECOND HARMONIC GENERATION

3.1 Nonlinear Susceptibility

The higher order interactions between electromagnetic (EM) waves and atomic matter describe the nonlinear response of matter to the EM waves. The high intensity and coherence of laser light sources makes observations of these processes possible. In second harmonic generation, $\omega_2 = 2\omega_1$, two fundamental photons are annihilated and one harmonic photon is created with energy of the field being conserved. This process is also referred to as coherent three photon scattering or three wave mixing. The macroscopic response of a medium is characterized by an induced nonlinear polarization

$$\mathbf{P}_{nls}(2\omega) = \boldsymbol{\chi}^{(2)}(2\omega;\omega,\omega): \mathbf{E}_{t}(\omega)\mathbf{E}_{t}(\omega), \qquad (3.1)$$

where \mathbf{E}_{t} is the macroscopic field in nonlinear response region, and $\chi^{(2)}$ the macroscopic second order susceptibility tensor.

For a centrosymmetric medium, the susceptibility tensor is invariant under the inversion operator. Elements of the rank three susceptibility tensor are

$$\chi^{(2)}_{abc} = \mathbf{a} \cdot \chi^{(2)} : \mathbf{bc},$$

where \mathbf{a} , \mathbf{b} , $\mathbf{c} = \mathbf{x}$, \mathbf{y} , \mathbf{z} . The invariance with respect to inversion results in

$$\boldsymbol{\chi}_{abc}^{(2)} = \mathbf{a} \cdot \boldsymbol{\chi}^{(2)} : \mathbf{b}\mathbf{c} = (-\mathbf{a}) \cdot \boldsymbol{\chi}^{(2)} : (-\mathbf{b})(-\mathbf{c}) = -\mathbf{a} \cdot \boldsymbol{\chi}^{(2)} : \mathbf{b}\mathbf{c} = -\boldsymbol{\chi}_{abc}^{(2)},$$

and suggests a zero second order nonlinear optical response. This conclusion can also be seen from the microscopic point of view. The rank three molecular susceptibility tensor can be determined through the expression from third-order perturbation theory^{24,25}

$$\beta_{abc}(2\omega;\omega,\omega) = \sum_{j,k} \left[\frac{\langle i|a|k\rangle \langle k|b|j\rangle \langle j|c|i\rangle}{(E_k - 2\hbar\omega - i\Gamma_k)(E_j - \hbar\omega - i\Gamma_j)} + \frac{\langle i|b|k\rangle \langle k|a|j\rangle \langle j|c|i\rangle}{(E_k + \hbar\omega - i\Gamma_k)(E_j - \hbar\omega - i\Gamma_j)} + \frac{\langle i|b|k\rangle \langle k|c|j\rangle \langle j|a|i\rangle}{(E_k + \hbar\omega - i\Gamma_k)(E_j + 2\hbar\omega - i\Gamma_j)} \right], \quad (3.2)$$

where $|i\rangle$ is the ground state and $|j\rangle$ and $|k\rangle$ are intermediate states. *E* and Γ are the eigen energy relative to E_i and the damping constant, respectively. Three time-ordered diagrams corresponding to the three terms in the summations of Eq.(3.2) are listed in Fig. 3.1.



Fig. 3.1 Three time-ordered diagrams of Eq.(3.2). (a) There are two possible resonance enhancements. (b) One possible resonance enhancement. (c) No possible resonance enhancement in this diagram since all the intermediate states have to be below the ground state.

If a molecule has inversion symmetry, then all its eigenstates, $|i\rangle$, $|j\rangle$, and $|k\rangle$, have to be labeled with either g or u. g means that the state is symmetric upon inversion, and u that it is antisymmetric. Since the electric dipole operator is an odd function, integrals for the transition moments in Eq.(3.2) are zero if the initial and final states are both g or both u. The third order processes described in Eq.(3.2) are forbidden because at least one of the three consecutive transitions is not allowed. For example, $g\rightarrow u\rightarrow g\rightarrow g$ is forbidden because the last transition is not allowed. However, introduction of an electric quadrupole or magnetic dipole transition moment may lead to a nonzero $\beta(2\omega;\omega,\omega)$ for a centrosymmetric matter.

Although it is prohibited in the centrosymmetric bulk within the electric dipole approximation, a second harmonic generation signal can rise from a very thin surface region of this medium because the symmetry is broken along the direction of the surface normal. This makes surface second harmonic generation (SSHG) an interesting surfacespecific probe for surface characterizations, surface phenomena, surface interactions etc., and for any interface accessible to light.²⁶ However, in a SSHG measurement, the detector collects the total signal from both the surface (electric dipole transition) and the bulk (electric quadrupole or magnetic dipole transition). The contribution of a surface nonlinear polarization to the SH field is less than that of a bulk nonlinear polarization roughly by a factor of $2\pi d/\lambda$,²⁷ where d is the thickness of the surface region and λ the optical wavelength. Meanwhile, the electric dipole transition moment is greater than the electric quadrupole and magnetic dipole transition moments by a factor of $\lambda/2\pi a$, where *a* is the dimension of the source of the multipole moments. Putting these two factors together, the surface contribution could at least have the same order of magnitude as the bulk contribution. The following calculations will concentrate primarily on the surface contribution within the electric dipole approximation.

The calculation of SSHG involves two distinct parts. The first is the determination of the nonlinear response, that consists of finding $\beta(2\omega;\omega,\omega)$. The second is to determine the actual microscopic fundamental and harmonic fields, given the applied field.

The macroscopic nonlinear susceptibility is related to its microscopic counterpart through the Lorentz local field factor for a medium of cubic symmetry.²⁵ The fundamental field is expressed as

$$\mathbf{E}_{\rm loc} = \mathbf{E}_{\rm mac} + \frac{4\pi}{3}\mathbf{P} = \mathbf{E}_{\rm mac} + \frac{4\pi}{3}N\alpha\mathbf{E}_{\rm loc}, \qquad (3.3)$$

where *N* is number density. The Lorentz-Lorenz relation provides the connection between the macroscopic dielectric constant (ϵ) and the microscopic polarizability (α), that is

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N\alpha. \tag{3.4}$$

By substituting Eq.(3.4) into Eq.(3.3), the Lorentz local field factor is defined as

$$\mathbf{E}_{\rm loc} = \frac{\varepsilon + 2}{3} \mathbf{E}_{\rm mac}$$

For the harmonic field, we have

$$(N\alpha)^{-1} \mathbf{P}_{\rm lin}^{2\omega} = \mathbf{E}_{\rm loc}^{2\omega} = \mathbf{E}_{\rm mac}^{2\omega} + \frac{4\pi}{3} \mathbf{P}_{\rm tot}^{2\omega} = \mathbf{E}_{\rm mac}^{2\omega} + \frac{4\pi}{3} \mathbf{P}_{\rm lin}^{2\omega} + \frac{4\pi}{3} \mathbf{P}_{\rm nl}^{2\omega}, \qquad (3.5)$$

where

$$\mathbf{P}_{nl}^{2\omega} = N\beta(2\omega;\omega,\omega): \mathbf{E}_{loc}^{\omega} \mathbf{E}_{loc}^{\omega}$$
(3.6)

is the source of the medium nonlinear response at 2ω . In Eq.(3.5) the local field at one lattice site has contributions from both the linear and nonlinear dipole moments at other sites. The interaction between nonlinear dipole moments at different lattice sites has been ignored (Eq.(3.6)) since the nonlinearity is considered as a small perturbation. By using the relationship in Eq.(3.4), Eq.(3.5) can be rearranged into

$$\mathbf{P}_{\rm lin}^{2\omega} = \frac{N\alpha^{2\omega}}{1 - \frac{4\pi}{3}N\alpha^{2\omega}} \mathbf{E}_{\rm mac}^{2\omega} + \frac{N\alpha^{2\omega}}{1 - \frac{4\pi}{3}N\alpha^{2\omega}} \frac{4\pi}{3} \mathbf{P}_{\rm nl}^{2\omega} = \frac{\varepsilon^{2\omega} - 1}{4\pi} \mathbf{E}_{\rm mac}^{2\omega} + \frac{\varepsilon^{2\omega} - 1}{3} \mathbf{P}_{\rm nl}^{2\omega}.$$

From this result, the macroscopic electric displacement field $D^{2\omega}$ can be expressed as

$$\mathbf{D}^{2\omega} = \mathbf{E}^{2\omega}_{\text{mac}} + 4\pi \mathbf{P}^{2\omega}_{\text{lin}} + 4\pi \mathbf{P}^{2\omega}_{\text{nl}} = \varepsilon^{2\omega} \mathbf{E}^{2\omega}_{\text{mac}} + \frac{\varepsilon^{2\omega} + 2}{3} 4\pi \mathbf{P}^{2\omega}_{\text{nl}},$$

$$\equiv \varepsilon^{2\omega} \mathbf{E}^{2\omega}_{\text{mac}} + 4\pi \mathbf{P}_{\text{nls}},$$
(3.7)

where \mathbf{P}_{nls} is the effective nonlinear source term for the Maxwell's equations. Compare Eqs.(3.1), (3.6) and (3.7), and we have

$$\chi^{(2)}(2\omega;\omega,\omega) = N\beta(2\omega;\omega,\omega)\frac{\varepsilon^{2\omega}+2}{3}\frac{\varepsilon^{\omega}+2}{3}\frac{\varepsilon^{\omega}+2}{3}.$$
(3.8)

3.2 Continuous Medium

With the expression of Eq.(3.7), two of the macroscopic Maxwell's equations for the harmonic fields in the nonlinear medium are

$$\nabla \times \mathbf{E}_{\text{mac}}^{2\omega} + \frac{1}{c} \frac{\partial(\mu \mathbf{H})}{\partial t} = 0, \text{ and}$$
$$\nabla \times \mathbf{H} = \frac{1}{c} \frac{\partial \mathbf{D}^{2\omega}}{\partial t} = \frac{1}{c} \frac{\partial(\varepsilon^{2\omega} \mathbf{E}_{\text{mac}}^{2\omega})}{\partial t} + \frac{4\pi}{c} \frac{\partial \mathbf{P}_{\text{nls}}}{\partial t}$$

Consider the nonmagnetic medium, $\mu=1$, and we have the inhomogeneous wave equation for the field at the harmonic frequency in the nonlinear medium,

$$\nabla \times \nabla \times \mathbf{E}_{\text{mac}}^{2\omega} + \frac{\varepsilon^{2\omega}}{c^2} \frac{\partial^2 \mathbf{E}_{\text{mac}}^{2\omega}}{\partial t^2} = -\frac{4\pi}{c^2} \frac{\partial^2 \mathbf{P}_{\text{nls}}}{\partial t^2}.$$
 (3.9)

3.2.1 Thin Slab Model

Bloembergen and Pershan²⁸ were the first to derive the analytical results of SSHG by considering a slab of nonlinear dielectric medium with boundaries at z = 0 and z = -d, embedded between two exclusively linear dielectrics (Fig. 3.2). The field in the nonlinear slab was taken from the solutions to Eq.(3.9). Boundary conditions were applied to both interfaces to determine the reflected (z > 0) and transmitted (z < -d) harmonic fields. They then took the limit of the slab thickness small compared to a wavelength and obtained the following results:

(I) reflected and transmitted fields in s-polarization:

$$E_r^{2\omega} = E_t^{2\omega} = i4\pi P_{nls}^{\perp} \left(\frac{2\omega d}{c}\right) \frac{1}{n^{2\omega}\cos\theta_m + \cos\theta},$$
(3.10)

(II) reflected field in p-polarization:

$$E_{r}^{2\omega} = -i4\pi P_{nis}^{\parallel} \left(\frac{2\omega d}{c}\right) \frac{\cos\theta_{m}\sin\alpha + \sin\theta_{m}\cos\alpha}{n^{2\omega}\cos\theta + \cos\theta_{m}},$$
(3.11)

(III) transmitted field in p-polarization:

$$E_{t}^{2\omega} = i4\pi P_{nls}^{\parallel}\left(\frac{2\omega d}{c}\right) \frac{\cos\theta\sin\alpha - \sin\theta_{m}\cos\alpha / n^{2\omega}}{n^{2\omega}\cos\theta + \cos\theta_{m}}.$$
 (3.12)

The nonlinear polarization components in the equations are defined by

$$\mathbf{P}_{\rm nls} = \mathbf{y} P_{\rm nls}^{\perp} + \mathbf{x} P_{\rm nls}^{\parallel} \sin \alpha + \mathbf{z} P_{\rm nls}^{\parallel} (-\cos \alpha), \qquad (3.13)$$

where α is the angle between the p-polarized \mathbf{P}_{nls} field and the negative z-axis. The scattering plane is the x-z plane. θ is the angle of incidence of the fundamental field and also the reflection angle of the harmonic field. This is because of the conservation of tangential component of wave vector, *e.g.* from Eq.(3.1), $e^{ik^{2\omega,x}x} = e^{ik^{\omega,x}x}e^{ik^{\omega,x}x} = e^{2ik^{\omega,x}x}$. Also because the vacuum has no dispersion, it follows that $(2\omega/c)\sin\theta^{2\omega} = k^{2\omega,x} = 2k^{\omega,x}$ $= 2(\omega/c)\sin\theta$ and that the reflection angle of the harmonic field $(\theta^{2\omega})$ equals θ . θ_m is the refraction angle at 2ω , and $\sin\theta = n^{2\omega}\sin\theta_m$ where $n^{2\omega}$ is the refractive index for 2ω .



Fig. 3.2 A thin slab model for surface second harmonic generation.

The reflected field in the vacuum has the Cartesian coordinate components

$$\mathbf{E}_{r}^{2\omega} = \mathbf{e}_{0+} E_{r}^{2\omega} = \mathbf{y} E_{r}^{2\omega,\perp} + \mathbf{x} E_{r}^{2\omega,\parallel} (-\cos\theta) + \mathbf{z} E_{r}^{2\omega,\parallel} \sin\theta.$$
(3.14)

Consider a diagonal tensor of Fresnel transmission coefficients for the field entering from the vacuum into a medium with refractive index *n* and refraction angle θ_m :

$$(\mathbf{L}^{\omega})^{yy} = \mathbf{t}^{\perp} = \frac{2\cos\theta}{\cos\theta + n^{\omega}\cos\theta_{m}}$$

$$(\mathbf{L}^{\omega})^{xx} = \mathbf{t}^{\parallel}(\frac{\cos\theta_{m}}{\cos\theta}) = \frac{2\cos\theta}{n^{\omega}\cos\theta + \cos\theta_{m}}(\frac{\cos\theta_{m}}{\cos\theta}) = \frac{2\cos\theta_{m}}{n^{\omega}\cos\theta + \cos\theta_{m}},$$
$$(\mathbf{L}^{\omega})^{zz} = \mathbf{t}^{\parallel}(\frac{\sin\theta_{m}}{\sin\theta}) = \frac{2\cos\theta}{n^{\omega}\cos\theta + \cos\theta_{m}}(\frac{\sin\theta_{m}}{\sin\theta}) = \frac{2\cos\theta}{n^{\omega}\cos\theta + \cos\theta_{m}}(\frac{1}{n^{\omega}}).$$

With expressions of Eq.(3.13) and Eq.(3.14), the reflected harmonic field in Eq.(3.10) and Eq.(3.11) becomes

$$\mathbf{E}_{r}^{2\omega} = i4\pi \left(\frac{\omega d}{c}\right) \frac{1}{\cos\theta} \left\{ \mathbf{L}^{2\omega} \cdot \boldsymbol{\chi}^{(2)}(2\omega;\omega,\omega) : [\mathbf{L}^{\omega} \cdot \mathbf{E}_{0}] [\mathbf{L}^{\omega} \cdot \mathbf{E}_{0}] \right\}.$$
(3.15)

For the electric field as a real quantity, we have

$$\mathbf{E}^{\omega}(t) = \mathbf{e}E^{\omega}e^{-i\omega t} + c.c. = \mathbf{e}(2|E^{\omega}|)\cos(\omega t).$$

The radiation power density associated with the electromagnetic field is the time average of the Poynting vector,

$$I_{\omega} = \frac{c}{4\pi} < |\mathbf{E}^{\omega}(t)|^{2} > = \frac{c}{\pi} |E^{\omega}|^{2} \frac{1}{T} \int_{0}^{T} \cos^{2}(\omega t) dt = \frac{c}{2\pi} |E^{\omega}|^{2},$$

and Eq.(3.15) can be converted into

$$I_{2\omega} = \frac{32\pi^3 \omega^2 d^2}{c^3} \sec^2 \theta [[\mathbf{e}_{0+} \cdot \mathbf{L}^{2\omega}] \cdot \boldsymbol{\chi}^{(2)}(2\omega; \omega, \omega): [\mathbf{L}^{\omega} \cdot \mathbf{e}_{0-}] [\mathbf{L}^{\omega} \cdot \mathbf{e}_{0-}]|^2 I_{\omega}^2,$$

where \mathbf{e}_{0} is the polarization unit vector for incident fundamental field, and \mathbf{e}_{0+} is for the harmonic reflected field. The volume polarization (dipole moments per unit volume) is usually written as surface polarization (dipole moments per unit area) for surface studies, $d \cdot \mathbf{P}_{nls} \rightarrow \mathbf{P}_{nls}$ or equivalently $d \cdot \boldsymbol{\chi}^{(2)} \rightarrow \boldsymbol{\chi}^{(2)}$. Then we reach the often quoted result of SSHG²⁹

$$I_{2\omega} = \frac{32\pi^3\omega^2}{c^3}\sec^2\theta [\mathbf{e}_{0+}\cdot\mathbf{L}^{2\omega}]\cdot\boldsymbol{\chi}^{(2)}(2\omega;\omega,\omega):[\mathbf{L}^{\omega}\cdot\mathbf{e}_{0-}][\mathbf{L}^{\omega}\cdot\mathbf{e}_{0-}]|^2I_{\omega}^2. \quad (3.16)$$

3.2.2 Nonlinear Polarization Sheet

Mizrahi and Sipe³⁰ took a different phenomenological approach. They treated the region that contributes to SSHG as an induced nonlinear polarization sheet sitting in

vacuum at $z = 0^+$ (Fig. 3.3). The nonlinear polarization sheet is induced by the fundamental field in the medium ($z = 0^-$) with a surface nonlinear susceptibility tensor $\chi^{(2)}(2\omega;\omega,\omega)$. The electromagnetic field generated by the induced dipole sheet, which is treated as a macroscopic source term, is obtained from a Green-function formalism.³¹ The reflected SSHG has two contributions, the directly generated upward-propagating wave and the downward-propagating wave reflected upward by the vacuum/medium interface at z = 0 (Fig. 3.3). The transmitted SSHG is just the downward-propagating wave picking up the Fresnel transmission coefficient at the interface. Their result in spolarization is identical to that of Eq.(3.10). Their p-polarization results are:

$$E_{r}^{2\omega} = -i4\pi P_{nls}^{\parallel} \left(\frac{2\omega}{c}\right) \frac{\cos\theta_{m}\sin\alpha + (n^{2\omega})^{2}\sin\theta_{m}\cos\alpha}{n^{2\omega}\cos\theta + \cos\theta_{m}} \quad \text{for reflection, and}$$
$$E_{t}^{2\omega} = i4\pi P_{nls}^{\parallel} \left(\frac{2\omega}{c}\right) \frac{\cos\theta\sin\alpha - n^{2\omega}\sin\theta_{m}\cos\alpha}{n^{2\omega}\cos\theta + \cos\theta_{m}} \quad \text{for transmission. When}$$

compared to Eqs.(3.11), (3.12) and (3.13), it is the contribution from *z*-component of nonlinear polarization, the $-P_{nls}^{\parallel} \cos \alpha$ term, that differs by a factor $(n^{2\omega})^2$. This discrepancy is the result of bringing the nonlinear polarization source outside the linearly responding medium. Recall that the tangential component of the electric field and the normal component of the displacement field ($\mathbf{D} = n^2 \mathbf{E}$) are continuous across the surface. The model considered by Mizrahi and Sipe is reasonable only when the nonlinearity arises mainly from molecules adsorbed on a surface and the local field factor of the molecules is negligible. The latter point may be justifiable if the surface coverage is so low that the effective dielectric constant of the adsorbing layer is very close to one.



Fig. 3.3 A nonlinear polarization sheet at $z = 0^+$ contributes to SSHG.

3.2.3 Nonlinear Dipole Sheet--A Semi-microscopic Model

We have taken another phenomenological approach to obtain the SSHG field by integrating the radiation field from a continuous sheet of nonlinear dipole moments. Each induced microscopic nonlinear dipole moment constituting the nonlinear dipole sheet inside the medium at $z = 0^-$ (Fig. 3.4) is

$$\mathbf{p}_{nl}(\mathbf{r}) = \beta(2\omega;\omega,\omega): [\mathbf{E}_{loc}e^{ik_x x}][\mathbf{E}_{loc}e^{ik_x x}]\delta(z-0^-), \qquad (3.17)$$
$$= \mathbf{p}p_{nl}e^{2ik_x x}\delta(z-0^-),$$

where **p** is the unit vector for the nonlinear dipole moment, $\mathbf{r} = (x, y, z)$, and the incident field is in the **x**-**z** plane so that $\mathbf{k} = (k_x, 0, k_z)$ with $k_x = (\omega/c)\sin\theta$ and $k_z = -(\omega/c)\cos\theta$. The electric local field in Eq.(3.17) can be the Lorentz local field or the numerical result of our complete microscopic treatment in Chapter II. The electric dipole field of this nonlinear dipole moment in a continuous medium of refractive index *n* at field frequency 2ω is¹³

$$\mathbf{E}_{dip} (\mathbf{R}, \mathbf{r}) = \frac{1}{n^2} \nabla \times \nabla \times \mathbf{p}_{nl} (\mathbf{r}) \frac{e^{iK|\mathbf{R}-\mathbf{r}|}}{|\mathbf{R} - \mathbf{r}|},$$
$$= \frac{K^2}{n^2} (\mathbf{n} \times \mathbf{p}_{nl}) \times \mathbf{n} \frac{e^{iK|\mathbf{R}-\mathbf{r}|}}{|\mathbf{R} - \mathbf{r}|} + [3\mathbf{n}(\mathbf{n} \cdot \mathbf{p}_{nl}) - \mathbf{p}_{nl}] (\frac{1 - iK|\mathbf{R} - \mathbf{r}|}{n^2 |\mathbf{R} - \mathbf{r}|^3}) e^{iK|\mathbf{R}-\mathbf{r}|},$$

where $K = (2\omega/c)n$. $\mathbf{n} = (\mathbf{R} - \mathbf{r})/|\mathbf{R} - \mathbf{r}| = \mathbf{R}'/R'$ is the unit radial vector with $\mathbf{R}' = (R_x - x, R_y - y, R_z - z)$. Since the field, either in reflection or the transmission, is observed far away

from the source point ($z = 0^{-}$), we could ignore terms of R^{1-2} and R^{1-3} , and the remaining is the typical radiation field.



Fig. 3.4 A nonlinear dipole sheet underneath the surface radiates at 2ω .

With N being the surface number density, the total radiation field from the nonlinear dipole sheet is

$$\mathbf{E}(\mathbf{R}) = N \iiint \mathbf{E}_{dip}(\mathbf{R}, \mathbf{r}) dx dy dz,$$
$$= N p_{nl} \left(\frac{2\omega}{c}\right)^2 \iint e^{2i(\omega/c)x \sin\theta} e^{i(2\omega/c)nR'} \frac{1}{R'} (\mathbf{n} \times \mathbf{p}) \times \mathbf{n} dx dy.$$
(3.18)

The double integrals in Eq.(3.18) can be solved by using the stationary phase approximation,¹⁴

$$\iint g(x,y)e^{ikf(x,y)}dxdy \approx \frac{2\pi i\sigma}{|\alpha\beta - \gamma|^{1/2}}g(x_0,y_0)\frac{e^{ikf(x_0,y_0)}}{k}.$$
 (3.19)

The approximation can be viewed as having the main contribution to the integral coming from some critical points (saddle and end points) if the amplitude g(x,y) changes more slowly than the phase term $e^{ikf(x,y)}$ along the integration path. In our case, the slope of the amplitude is $1/R^{12}$ while the slope of phase term is in the order of $k = 2\pi/\lambda$. As long as we detect the field several wavelengths away, the condition $1/R^{12} << 2\pi/\lambda$ is satisfied. In

Eq.(3.19), the critical point
$$(x_0, y_0)$$
 satisfies the conditions $(\frac{\partial f}{\partial x}) = (\frac{\partial f}{\partial y}) = 0$.
The other parameters are: $\alpha \equiv (\frac{\partial^2 f}{\partial x^2})_{x=x_0}$, $\beta \equiv (\frac{\partial^2 f}{\partial y^2})_{y=y_0}$, $\gamma \equiv (\frac{\partial^2 f}{\partial x \partial y})_{\substack{x=x_0, y=y_0}}$

and
$$\sigma = \begin{cases} +1 & \text{for } \alpha\beta > \gamma^2 \text{ and } \alpha > 0, \\ -1 & \text{for } \alpha\beta > \gamma^2 \text{ and } \alpha < 0, \\ -i & \text{for } \alpha\beta < \gamma^2. \end{cases}$$

From Eq.(3.18), since $f(x, y) = n[(R_x - x)^2 + (R_y - y)^2 + R_z^2]^{1/2} + x \sin\theta$, we find

$$\frac{\partial f}{\partial y} = \frac{n}{2R'}(-2)(R_y - y) \Longrightarrow y_0 = R_y \text{ and } \left(\frac{\partial f}{\partial x}\right)_{y=y_0} = -\frac{n}{R'}(R_x - x) + \sin\theta$$

$$\Rightarrow n(R_x - x_0) = \sqrt{(R_x - x_0)^2 + R_z^2} \sin \theta \Rightarrow R'_{0x} = R_x - x_0 = \frac{|R_z|\sin \theta}{\sqrt{n^2 - \sin^2 \theta}} = |R_z|\tan \theta_m$$
$$\Rightarrow R'_0 = R'|_{x_0, y_0} = |R_z| \sqrt{\frac{\sin^2 \theta}{n^2 - \sin^2 \theta} + 1} = \frac{|R_z|}{\cos \theta_m}.$$

Snell's law, $\sin \theta = n \sin \theta_m \Rightarrow n^2 - \sin^2 \theta = n^2 \cos^2 \theta_m$, has been applied. We also have

$$\alpha = \frac{(n^2 - \sin^2 \theta)^{3/2}}{n^2 |R_z|} = \frac{n \cos^3 \theta_m}{|R_z|}, \ \beta = \frac{n \cos \theta_m}{|R_z|}, \ \gamma = 0, \ \text{and} \ \sigma = 1. \ \text{Eq.}(3.18) \ \text{becomes}$$
$$\mathbf{E}(\mathbf{R}) \approx \frac{N p_{\text{nl}} (2\omega/c)^2 2\pi i |R_z|}{n \cos^2 \theta_m (2\omega/c)} e^{i(2\omega/c)f(x_0, y_0)} g(x_0, y_0),$$
$$= \frac{N p_{\text{nl}} (2\omega/c) 2\pi i R'_0}{n \cos \theta_m} e^{i(2\omega/c)(R_z |\sqrt{n^2 - \sin^2 \theta} + R_z \sin \theta)} \frac{1}{R'_0} (\mathbf{n}_0 \times \mathbf{p}) \times \mathbf{n}_0,$$
$$= \frac{N p_{\text{nl}} (2\omega/c) 2\pi i R}{n \cos \theta_m} e^{iK_m^* \cdot \mathbf{R}} [\mathbf{p} - (\mathbf{n}_0 \cdot \mathbf{p})\mathbf{n}_0], \qquad (3.20)$$

where $\mathbf{n}_0 = (R'_{0x}/R'_0, 0, R_z/R'_0) = (\sin\theta_m, 0, \pm \cos\theta_m)$ and, incidentally, also $\mathbf{K}_m^{\pm} = K(\sin\theta_m, 0, \pm \cos\theta_m)$. The plus sign and the minus sign refer to upward $(R_z > 0^-)$ and downward $(R_z < 0^-)$ propagation, respectively. The "reflected" harmonic field in vacuum is the transmitted collective dipole field in Eq.(3.20) through the medium/vacuum interface (Fig. 3.4). The "transmitted" harmonic field in the medium has contributions from the downward-propagating dipole field and the reflection at the interface of the upward-propagating dipole field. Fresnel transmission and reflection coefficients for waves traveling from the medium of index *n* to the vacuum are:

$$\mathbf{t}_{n0}^{\perp} = \frac{2n\cos\theta_m}{\cos\theta + n\cos\theta_m}, \qquad \mathbf{r}_{n0}^{\perp} = \frac{n\cos\theta_m - \cos\theta}{\cos\theta + n\cos\theta_m},$$
$$\mathbf{t}_{n0}^{\parallel} = \frac{2n\cos\theta_m}{n\cos\theta + \cos\theta_m}, \qquad \mathbf{r}_{n0}^{\parallel} = \frac{\cos\theta_m - n\cos\theta}{n\cos\theta + \cos\theta_m}.$$

For s-polarized dipole moments, $\mathbf{p} = \mathbf{y}$ and $\mathbf{n}_0 \cdot \mathbf{y} = 0$, the field amplitude of

Eq.(3.20) is
$$E_{\pm}^{\perp} = \frac{Np_{nl}^{\perp}(2\omega/c)2\pi i}{n\cos\theta_{m}}$$
 with $\mathbf{e}^{\perp} = \mathbf{y}$. We then have
 $E_{\tau}^{\perp} = E_{\pm}^{\perp} \mathbf{t}_{n0}^{\perp} = \frac{Np_{nl}^{\perp}(2\omega/c)4\pi i}{\cos\theta + n\cos\theta_{m}}$ and also

$$E_{\tau}^{\perp} = E_{-}^{\perp} + E_{+}^{\perp} \mathbf{r}_{n0}^{\perp} = \frac{N p_{n1}^{\perp} (2\omega/c) 4\pi i}{\cos\theta + n\cos\theta_{m}}.$$
 (3.21)

For p-polarized dipole moments, $\mathbf{p} = \mathbf{x}\sin\alpha - \mathbf{z}\cos\alpha$ (see Eq.(3.13)), then

$$\mathbf{p} - (\mathbf{n}_0 \cdot \mathbf{p})\mathbf{n}_0 = \mathbf{x}\sin\alpha - \mathbf{z}\cos\alpha - (\sin\theta_m \sin\alpha \mp \cos\theta_m \cos\alpha)(\mathbf{x}\sin\theta_m \pm \mathbf{z}\cos\theta_m)$$
$$= (\mathbf{x}\cos\theta_m \mp \mathbf{z}\sin\theta_m)\cos\theta_m \sin\alpha - (\mp \mathbf{x}\cos\theta_m \sin\theta_m + \mathbf{z}\sin^2\theta_m)\cos\alpha.$$

Since the p-polarization vector for the electric field propagating in the medium is $\mathbf{e}_{\pm}^{\parallel} = (\mp \mathbf{x} \cos \theta_m + \mathbf{z} \sin \theta_m)$, we have as the field amplitude of Eq.(3.20)

$$E_{\pm}^{\parallel} = \frac{Np_{nl}^{\parallel}(2\omega/c)2\pi i}{n\cos\theta_{m}} [\mathbf{p} - (\mathbf{n}_{0} \cdot \mathbf{p})\mathbf{n}_{0}] \cdot \mathbf{e}_{\pm}^{\parallel}$$
$$= \frac{Np_{nl}^{\parallel}(2\omega/c)2\pi i}{n\cos\theta_{m}} (\mp\cos\theta_{m}\sin\alpha - \sin\theta_{m}\cos\alpha).$$

After applying the Fresnel coefficients, the harmonic field reflected from the medium is

$$E_{\rm r}^{\rm H} = E_{\rm +}^{\rm H} t_{n0}^{\rm H} = -Np_{\rm nl}^{\rm H} (2\omega/c) 4\pi i \frac{\cos\theta_{\rm m}\sin\alpha + \sin\theta_{\rm m}\cos\alpha}{n\cos\theta + \cos\theta_{\rm m}}; \qquad (3.22)$$

and the transmitted harmonic field in the medium is

$$E_{t}^{\parallel} = E_{-}^{\parallel} + E_{+}^{\parallel} r_{n0}^{\parallel} = N p_{nl}^{\parallel} (2\omega/c) 4\pi i \frac{\cos\theta \sin\alpha - \sin\theta_{m} \cos\alpha/n}{n\cos\theta + \cos\theta_{m}}.$$
 (3.23)

The results in Eqs.(3.21)-(3.23) have the same angular dependence as those in Eqs.(3.10)-(3.12). But the over all magnitude is off by a Lorentz local field factor

 $((\epsilon^{2\omega} + 2)/3)$ due to the difference between P_{nls} and Np_{nl} (see Eq.(3.7)). This error originates in the negligence of the dipolar interaction in the linear medium responding to the dipole field of the nonlinear dipole moments. When a macroscopic field is to be related to the corresponding microscopic field, it requires a self-consistent approach (*e.g.* Eqs.(3.3) and (3.5)). Unfortunately, this is exactly what we did not do in Eq.(3.18).

3.3 Microscopic Calculations of SSHG

Several research groups³²⁻³⁵ have pursued the complete microscopic treatment of SSHG. In a discrete dipole approach with the electric dipole field calculated in the Lorentz gauge, Wijers et al.³² calculated the reflected SSHG from a Si(110) thin slab (number of layers: 32 to 79) as a function of the angle of incidence. They found that SSHG and SIOA, surface induced optical anisotropy, turned out to be closely related phenomena. However the p-polarized SSHG, unlike SIOA, showed a high sensitivity for the shape of the surface layer polarizability matrix. Munn et al.33 developed a microscopic theory of nonlinear optical response in an assembly of ordered molecular layers. Their local field calculation is formulated in the Coulomb gauge so that the knowledge of the macroscopic field is needed. They also calculated the nonlinear susceptibility $\chi^{(2)}$ of model Langmuir-Blodgett films³⁴ by treating the molecules as a string of beads. Their results showed that the tilt of the string away from the normal to the film had a major effect on the pattern of components of $\chi^{(2)}$ tensor. The SSHG of Langmuir-Blodgett monolayer was also the subject of a study by Cnossen et al.³⁵ They attributed the deviation from a linear dependence of SSHG with increasing surface density in their systems to the local field effects. In the calculation of the local field for a partially ramdon oriented system, they used an iterative procedure combined with a Monte Carlo technique. For a crystallike model, the result of a lattice summation of a

monolayer was adopted to give an analytical expression. Their results showed that both models manifested qualitatively the same nonlinear behavior of SSHG *versus* surface density, despite the fact that the calculated local fields for the two models were different.

3.3.1 The Self-consistent Calculation and Results

Following the microscopic calculation of the linear response at the fundamental frequency in previous chapter, we can simply repeat the whole process at the harmonic frequency with the external field replaced by the dipole fields from the nonlinear dipole moments. It is assumed that only the topmost surface layer has a nonzero microscopic second order susceptibility tensor $\beta(2\omega;\omega,\omega)$ because of the broken symmetry in the direction of the surface normal. A nonlinear dipole moment for SSHG subjected to the local field $\mathbf{E}_{ioc}(\omega, (z = 0))$, which deviates from the bulk value, can be evaluated through

 $\mathbf{p}_{nl}(2\omega) = \beta(2\omega; \omega, \omega): [\mathbf{\alpha}_{0}^{i,j}(\omega) \cdot \mathbf{p}_{i=0}(\omega)] [\mathbf{\alpha}_{0}^{i,j}(\omega) \cdot \mathbf{p}_{i=0}(\omega)],$ (3.24) where $\mathbf{p}_{i=0}(\omega)$ is the numerical result from Eqs.(2.67) and $\mathbf{\alpha}_{0}(\omega)$ the polarizability tensor of the topmost surface layer. $\mathbf{p}_{nl}(2\omega)$ then becomes the source of an applied harmonic field. With a given $\mathbf{\alpha}_{b}(2\omega)$, $\psi_{h}(2\omega)$ and $\mathbf{u}_{h}(2\omega)$ can be found for the bulk response as in the linear calculation. In Eq.(2.67a), the external plane wave at the surface layer *i*, $\mathbf{E}_{0}e^{i\mathbf{k}\cdot\mathbf{r}_{i}}$, is replaced by the electric dipole field. $\mathbf{F}_{i0}(2\omega)\cdot\mathbf{p}_{nl}(2\omega)$, generated by the nonlinear dipole moments at *i* = 0. In Eqs.(2.67b) and (2.67c), the external field amplitude, \mathbf{E}_{0} , in the bulk region is replaced by the downward long range dipole field $\mathbf{B}_{00}(2\omega)\cdot\mathbf{p}_{nl}(2\omega)$. Only the contribution of p = q = 0 term is needed if the bulk region is at least five layers away from the source dipole layer ($L \ge 5$) in the long wavelength applications (see the numerical results in Table 2.4). With $\mathbf{\alpha}_{i}$ being the polarizability tensor for the surface layers at the harmonic frequency, we can again obtain the dipole moments $\mathbf{p}_{i}(2\omega)$ and $v_{h}(2\omega)$ self-consistently from the simultaneous linear equations:

$$\sum_{j=0}^{L} \left[\boldsymbol{\alpha}_{i}^{-1} \boldsymbol{\delta}_{ij} - \mathbf{F}_{ij} \right] \cdot \mathbf{p}_{j} - \sum_{h=0}^{1} v_{h} \sum_{p,q} \mathbf{D}_{pq} \cdot \mathbf{u}_{h} \frac{e^{i\kappa_{pq}(z_{i}-z_{L}+a)}}{1 - e^{i(\kappa_{pq}-\psi_{h})a}} = \mathbf{F}_{i0} (2\omega) \cdot \mathbf{p}_{nl} (2\omega), \quad (3.25a)$$
$$-\sum_{i=0}^{L} \mathbf{u}_{0} \cdot \mathbf{B}_{00} e^{i\kappa_{00}z_{j}} \cdot \mathbf{p}_{i} + \sum_{h=0}^{1} v_{h} \frac{\mathbf{u}_{0} \cdot \mathbf{B}_{00} \cdot \mathbf{u}_{h}}{e^{-i(\kappa_{pq}+\psi_{h})a} - 1} e^{-i\kappa_{00}(a-z_{L})} = \mathbf{u}_{0} \cdot \mathbf{B}_{00} \cdot \mathbf{p}_{nl} (2\omega), \quad (3.25b)$$
$$-\sum_{i=0}^{L} \mathbf{u}_{1} \cdot \mathbf{B}_{00} e^{i\kappa_{00}z_{j}} \cdot \mathbf{p}_{i} + \sum_{h=0}^{1} v_{h} \frac{\mathbf{u}_{1} \cdot \mathbf{B}_{00} \cdot \mathbf{u}_{h}}{e^{-i(\kappa_{pq}+\psi_{h})a} - 1} e^{-i\kappa_{00}(a-z_{L})} = \mathbf{u}_{1} \cdot \mathbf{B}_{00} \cdot \mathbf{p}_{nl} (2\omega). \quad (3.25c)$$

Then the reflected harmonic field off the surface is

$$\mathbf{E}_{r}(2\omega) = \mathbf{D}_{00} \cdot \mathbf{p}_{n1}(2\omega) + \sum_{i=0}^{L} \mathbf{D}_{00} \exp(-i\kappa_{00}z_{i}) \cdot \mathbf{p}_{i}(2\omega)$$
$$+ \sum_{h=0}^{1} v_{h} \mathbf{D}_{00} \cdot \mathbf{u}_{h} \frac{\exp[i\kappa_{00}(-z_{L}+a)]}{1 - \exp[-i(\psi_{h} - \kappa_{00})a]}.$$
(3.26)

The first term in the last equation is the upward dipole field of the nonlinear dipole moments. The next two terms are contributions of the surface layers and the bulk linear responses to the downward dipole field of the nonlinear dipole moments.

Results of Eq.(3.26) are compared with the macroscopic results of Eq.(3.15) for a system of equivalent refractive indices $n^{\omega} = 2.5$ and $n^{2\omega} = 3.0$, with both the incident and outgoing fields having p-polarization. In Fig. 3.5, $\beta_{zzz} = 50 \times 10^{-30}$ esu is the only nonzero tensor element for the calculation. The number is typical for dielectric and molecular materials with a large nonlinearity.³⁶ In some cases, the surface has a lower symmetry, like C_{2v}, than the isotropic bulk. There are seven nonzero elements in that surface susceptibility tensor. In Fig. 3.6, they are $\beta_{xzx} = \beta_{xzx} = -50 \times 10^{-30}$ esu, and β_{yyz} $= \beta_{yzy} = \beta_{zxx} = \beta_{zyy} = \beta_{zzz} = 50 \times 10^{-30}$ esu for the calculation. Our numerical results of the SSHG calculations show a similar angular dependence compared to the analytial macroscopic results, despite the discrepancy in the magnitude which is inherited from the difference in the local fundamental field. This discrepancy demonstrates the importance of the local field analysis in interpreting the microscopic nonlinear susceptibility from the experimental measurement or *vice versa*.



Fig. 3.5 The reflected surface harmonic field (pp) with a nonzero β_{zzz} . pp : both the incident and outgoing fields are in p-polarization. The fundamental field amplitude is $|\mathbf{E}_0| = 1$. Eq.(3.15) is used to calculate the macroscopic result (the square) and Eq.(3.26) for the line.



Fig. 3.6 The reflected surface harmonic field (pp) with seven nonzero tensor elements ($C_{2\nu}$). All the other calculation conditions are the same as that of Fig. 3.5.

Since the tangential components of the surface local field deviate from the bulk result more than the normal component does (see Fig. 2.8 and Fig. 2.9), the nonlinear dipole moment of Eq.(3.24) should be different from the effective nonlinear polarization \mathbf{P}_{ais} of Eqs.(3.1 and 3.8) not only in the magnitude but also in the orientation. The latter is the angle α in Eqs.(3.11 to 3.13), which varies with the incident angle θ . Although α behaves differently in \mathbf{p}_{nl} and \mathbf{P}_{ais} against θ , the θ dependences of SSHG, as shown in Fig. 3.5 and Fig. 3.6, are still quite similar between the two calculations. In some cases (combinations of nonzero β tensor elements), the angles of the maximum SSHG in the two calculations can differ by 1°, but the overall angular dependences are dominated by the Fresnel coefficients at the fundamental and harmonic frequencies. The Fresnel coefficients are the bulk properties and have no difference in the two models.

3.4 Conclusion

The nonlinear dipole moments at the harmonic frequency arise at the surface of a centrosymmetric medium because of the breaking of symmetry. The surface local fundamental field and the nonlinear susceptibility tensor determine the nonlinear dipole moments. Since the cross section of the nonlinear process is small in general, the interaction between the nonlinear dipole moments is ignored in our treatment. That is, no energy loss in the fundamental field has been considered when the nonlinear dipole moments are created. Meanwhile, the dipolar interaction between the linear dipole moments at the harmonic frequency in the medium requires a self-consistent treatment in order to obtain the correct medium response to the electric dipole fields of the nonlinear dipole moments. Calculations of SSHG of nonlinear dipole moments generated by the surface local fundamental field and by the bulk local fundamental field (macroscopic model) only differ in the magnitude of SSHG. The angular dependency of SSHG is dominated by the Fresnel's law of reflection and transmission.

For a system consisting of multiple layers of different linear and nonlinear polarizability tensors, the macroscopic model becomes very difficult by solving the multi-boundary problem. On the other hand, the microscopic calculation is much simpler to obtain a numerical result for this complicate system. The self-consistent solution will follow the additions of the induced nonlinear dipole moments (similar to that of Eq.(3.24)) of various layers to the right-hand side of Eqs.(3.25), as the source terms, with the correct dipolar interaction operators.

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CHAPTER IV

EXPERIMENTS WITH SURFACE SECOND HARMONIC GENERATION

4.1 Apparatus

4.1.1 Laser and Optics

Since the output of second harmonic generation is quadratic in the power density of incident radiation, intense laser pulses are required to generate measurable signals. Experiments were performed with a Nd:YAG (neodymium +3 ions doped in yttrium aluminum garnet) laser system (Quantronix model 116). The continuous wave (CW) power in the TEM₆₀ mode was 8 Watts, at 1064 nanometers (nm). When Q-switching the average power was 1 Watt at 500 Hz repetition rate. Another intracavity modulator (mode locker), also driven by 5-10 Watts of RF at 50 MHz, generates trains of approximately 30 pulses spaced by 10 nanoseconds (ns) and having a duration of 100 ps (picoseconds). While the shape of the Q-switched pulse depends on the power of RF applied to the modulator, which is just a fused silica wedge, the typical pulse envelope is about 400 ns. More than 95% of intensity of the pulse train is contained in 30 modelocked pulses, and this is the factor we use to estimate the pulse average power density. The peak ML-pulse is about 1/20 of the fluence of the entire Q-switched pulse train. The linearly polarized output radiation is produced by a thin optic flat positioned at Brewster's angle inside the laser cavity.

The IR radiation is frequency doubled to obtain green light at 532 nm. Two frequency doubling crystals have been used, KD*P (KD_2PO_4 Potassium Dideuterium Phosphate) and CD*A (CsD_2AsO_4 Cesium Dideuterium Arsenate), with conversion



Fig. 4.1 Diagram of the experimental apparatus.

efficiencies ranging from 25% to 35%. Both crystals were arranged for type I phase matching so that the polarizations of IR and green were perpendicular to each other. The two beams were separated by a calcite polarizer and a harmonic beam splitter. Phase matching was achieved at room temperature by angle tuning, resulting in beam "walk-off",³⁷ for the KD*P crystal. We were able to damage the KD*P crystal with a power density greater than 100 GW/cm² of IR. The CD*A crystal, on the other hand, was temperature-tuned at around 106°C to achieve phase matching at 90 degrees to the optic axis. This 300 to 400 mW of green was the fundamental field for our surface second harmonic generation experiments.

Two fresnel rhombs were set up to intercept the green before it was sent to bounce off the sample surface. Each fresnel rhomb served as a quarter wave plate. The first one converted the linearly polarized light into circularly polarized and the second converted it back into linearly polarized but 90° to its original polarization. This allowed us to rotate input polarizations, either p or s, conveniently. The angle of incidence on the sample was 45°. Since the second harmonic generation is a coherent process, the signal emerges as a beam from the sample instead of scattered photons with a wide solid angle. Lenses with long focal lengths, 35 to 50 cm, were used to focus the green onto the sample. This was done to avoid signals arising from the windows of the vacuum chamber and also to allow the detector to be set farther away from the sample so that photons of incoherent scattering processes, *e.g.* two photon induced fluorescence, did not interfere with detecting the UV SHG photons.

The SSHG signal (UV at 266 nm) and the reflected green propagated collinearly and were separated by a dielectric mirror, which reflected 90% of 266 nm at 45° angle of incidence while transmitting the most of the 532 nm. The linear reflectance of the sample was constantly monitored through this transmitted green beam by a photodiode. The UV beam was then directed through several pieces of color filter glass (Schott UG-5, 45% transmission at 266 nm) to remove the residual green photons. A calcite polarizer (less than 40% transmission at 266 nm) was added in the beam path to analyze the s and p components of the UV signal when needed. A fused silica lens (50% transmission at 266 nm) focused the UV photons onto a bialkali (K_2 CsSb) cathode photomultiplier tube (PMT, Hamamatsu R372, 20% quantum efficiency at 266 nm, 2.0×10^7 gain). The negative current of the PMT was integrated over each Q-switched pulse train. After further amplification, the signal of each pulse train was passed through an analog-to-digital converter (ADC, 12 bits, 0-10 volts, 2.5 mV per count) and recorded and normalized in a computer. The normalization was done by using a UV reference beam generated from a KD*P crystal.

4.1.2 Signals

Consider a green beam with an average power of 50 mW focused into a spot with a diameter of 100 μ m. The photon energy is $hc/\lambda \approx 3.7 \times 10^{-19}$ joules/photon, and we have:

energy per Q-switched pulse = 50×10^{-3} joules/ $500 = 10^{-4}$ joules;

photons per Q-switched pulse = 2.7×10^{14} ;

energy per mode locked pulse = 10^{-4} joules/ $30 = 3.3 \times 10^{-6}$ joules;

photons per mode locked pulse = 9.0×10^{12} .

With a pulse duration of 100 ps and a sampling area of $\pi r_0^2/\cos\theta \approx 1.1 \times 10^{-4} \text{ cm}^2$, the average applied single pulse power density is 300 MW/cm² or $3 \times 10^{15} \text{ ergs}/(\text{sec} \cdot \text{cm}^2)$. If we ignore the local field factors and the angle dependent transmission coefficients ($n(\omega) \approx n(2\omega) \approx 1$), the average power density of UV from a sample of $\beta = 0.5 \times 10^{-30} \text{ esu}$, which is a well-known value for urea ((NH₂)₂CO), and number density $N \approx 1.6 \times 10^{15} \text{ cm}^{-2}$

is
$$I_{2\omega} \approx \frac{32\pi^3 \omega^2}{c^3} |N\beta|^2 I_{\omega}^2 \approx 2.4 \times 10^3 \text{ ergs/(sec} \cdot \text{cm}^2)$$
. After multiplying the pulse

duration and the sampling area, the average SSHG signal we expect to observe is: energy per mode locked pulse = 2.7×10^{-11} ergs; photons per mode locked pulse = 3.5;

photons per Q-switched pulse = 1.1×10^2 .

The integrated signal of each shot (a Q-switched pulse) is estimated as following: 100 (photons) \div 200 (loss through window, beam splitter, color filters, lens *etc.* before reaching PMT) \times 20% (e/photon) \times 2 \times 10⁷ (gain of PMT) \times 1.6 \times 10⁻¹⁹ (coul/e⁻) \div 10⁻⁹ (farad, capacitance of integrator) \times 60 (electronic amplification) = 19 mV. The signal levels we had encountered were usually 10 to 100 times bigger than this.

4.1.3 Beam Size

As we have used in the previous estimation, the second order nonlinear signal is inversely proportional to the sampling area. The focused incident beam size becomes a handy adjustable parameter to maximize the harmonic signal before damaging the sample. In order to estimate the incident power density, a razor blade was set up on a translation stage, traveling across the beam, to measure the beam diameter. For I_0 the power density at the center of the Gaussian beam profile and r_0 the radius (1/*e*), the total power is obtained by the integration over the two dimensional Gaussian distribution,

$$Q = \int_0^\infty I_0 e^{-r^2/r_0^2} 2 \pi r dr = \pi r_0^2 I_0.$$

When the razor blade is moved toward the center of the beam, the residual power measured behind the blade is

$$Q'(s) = \int_0^s I_0 e^{-r^2/r_0^2} 2\pi r dr + \int_s^\infty I_0 e^{-r^2/r_0^2} (2\pi - \theta) r dr$$

where s is the distance between the blade and center of the beam. θ is $2\cos^{-1}(s/r)$ and, as s approaches zero, Q'(0) = Q/2. These two integals in the last expression can be rearranged into

$$Q'(s) = \int_0^\infty I_0 e^{-r^2/r_0^2} 2\pi r dr - \int_s^\infty I_0 e^{-r^2/r_0^2} \Theta r dr = Q - \int_s^\infty I_0 e^{-r^2/r_0^2} 2r \cos^{-1}(s/r) dr$$

We have the residual power fraction

$$f(s) = \frac{Q'(s)}{Q} = 1 - \frac{2\int_{s}^{\infty} e^{-r^{2}/r_{0}^{2}} r \cos^{-1}(s/r) dr}{\pi r_{0}^{2}},$$

or $f(n) = 1 - (2/\pi) \int_{n}^{\infty} e^{-x^{2}} x \cos^{-1}(n/x) dx$, where $s = nr_{0}$ and $r = xr_{0}$. Numerical results of this fraction function have f(1) = 0.921351, f(0.5) = 0.760251, f(0.2) = 0.611354, f(0.1) = 0.556234, f(0.01) = 0.505647. According to this analysis, the beam

diameter (1/e) can be determined by the displacement of the blade between 92% and 8% of the residual power measured behind it.

The Gaussian beam waist of a tightly focused spot w_0 , with lens of focal length f, can also be estimated as $w_0 = \frac{\lambda f}{\pi w_s}$, where w_s is the beam diameter at the lens and λ the wavelength.

4.1.4 Photon Detection

Using the parameters listed in section 4.1.2, we can estimate the signal level of one single photoelectron event in our detecting system as 192 mV, which will register 77 counts from the ADC. Fig. 4.2 to Fig. 4.5 are the histograms of different signal levels of photons sent into the PMT. Each one was the accumulation of 200,000 shots with a bin size of one count. Fig. 4.2 had a signal level less than 250 mV, which was monitored by a voltmeter in the input of ADC, and became an ideal example of single-photoelectron distribution. The giant spike at 71 of 50,323 peak counts and about 8 ADC-counts wide was the result of PMT dark current and electronic offset. This was related to a 160-170 mV of background noise when there was no light input to the PMT. The noise arising from PMT dark current had been reduced tremendously by using a gated integrator.



Fig. 4.2 Single-photoelectron distribution of 200,000 events (250 mV) collected by a PMT. The signal level was about 80 mV above the background.



Fig. 4.3 Histogram of 200,000 events (400 mV). The signal level was about 250 mV above the background. The two-photoelectron distribution also became probable in the statistics.







Fig. 4.5 Histogram of 200,000 events (600 mV). The signal level was about 400 mV above the background.

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The little feature to the right, 72 ADC-counts away, demonstrated the Poisson distribution, although not exactly,³⁸ of the secondary electron emissions from the successive dynodes in the PMT. The signal level in Fig. 4.3 was 350-500 mV. A small shoulder at 226 ADC-counts, about 83 away from the first bump, represented the increasing probability of a two-photoelectron response. Another PMT, which had higher dark current and slightly lower gain, was tested and the results are shown in Fig. 4.4 (350-500 mV) and Fig. 4.5 (500-700 mV). The base line moved up to 95 and the single-photoelectron response was about 35 ADC-counts. As the signal level increases, the distribution becomes more and more symmetric (Fig. 4.5). The width of the distributions in the histograms characterized the noisy nature of the detected signal. An averaging process was required to increase the signal-to-noise ratio. Typically, 500-4,000 shots were accumulated to obtain an averaged data point.

4.2 Rutile

Titanium dioxide exists as rutile, anatase and brookite, with rutile being the thermodynamically stable form at standard conditions. The unique photodynamics and its applications to protective surface coatings, photocatalysis *etc.*, have made this transition metal oxide an extensively studied material. Rutile TiO_2 has a band gap of 3.05 eV (407 nm). It is yellowish in color and transparent in the visible range. The bulk symmetry of rutile is D_{4h} , which includes inversion symmetry. Because there is no bulk signal in the electric dipole approximation, rutile is an ideal candidate for surface second harmonic generation studies.

A rutile prism was set in a stainless steel chamber with a base pressure of less than 10⁻⁸ torr when pumped by an ion pump. The pressure was not able to go below this point because there were two viton o-rings to seal two high optical quality fused silica windows. These windows had to allow the fundamental beam to pass into the vacuum chamber while preserving the beam quality, and the UV to pass out of the chamber with low loss. We avoided the use of commercial UHV (ultra high vacuum) windows because the metal/glass seal distorted the optical quality of the window. The crystal surface we studied was the (001) surface subjected to a fine optical polish. The first experiment we tried on this rutile prism was to determine how much laser intensity we could apply to generate a large enough SSHG signal without damaging the surface. The photo-ablation threshold was estimated to be about 490 MW/cm² in vacuum environment and about 650 MW/cm² when 1 torr of oxygen was present, using the 100 ps laser pulses.

The SH signal is supposed to vary with the incident power quadratically. In order to verify this relationship four neutral density filters (82%, 65%, 42%, and 10% transmission) were used to attenuate the incident beam. The reference beam for signal normalization was not attenuated. The resulting power dependency, expressed as signal *versus* I_{ω}^{n} , was n = 1.9 ± 0.2.

4.2.1 Surface Symmetry and SSHG

There are 18, out of 27 total, possible independent elements of the surface susceptibility tensor $\chi^{(2)}(2\omega;\omega,\omega)$ because of the degeneracy of the two input photons. However, the actual number of independent nonvanishing elements is dependent on the symmetry of the surface. The polarization dependent measurements of SSHG are thus a way to probe the symmetry information about the surface. We refer to the total SH signals arising from p-polarized and s-polarized fundamental beams as p-total and s-total, and their polarization components as pp, ps and sp, ss, respectively, where the first letter refers to the fundamental and the second to the harmonic. Ideally, p-total should be the sum of pp and ps, multiplied by the attenuation factor of the analyzing polarizer. And, stotal signal should be the sum of sp and ss multiplied by the attenuation factor of the analyzing polarizer. In Table 4.1, the independent nonvanishing elements of $\chi^{(2)}(2\omega;\omega,\omega)$ for several surface symmetry classes and their contributions to the polarization dependent SH signals are listed. The listed tensor elements are similar, but with a few corrections, to those given in reference.²⁷

Either C_{4v} or C_{2v} are the possible surface symmetries of a bulk with D_{4h} symmetry. Our sample was a mechanically polished surface, not a single crystal surface, and it was supposed to be random and rough on the microscopic scale. The polarization dependent SH signals, in arbitrary units, are shown in Fig. 4.6, for a vacuum environment, and in Fig. 4.7, for an oxygen environment. A Schott KG-4 color glass filter, which transmits visible and rejects UV, was used to establish the base line of the signal level from the PMT. Both ps and ss components were not zero, which could be due to the contribution from the electric quadrupole or magnetic dipole transition moments in the bulk $\chi^{(2)}$. In order to obtain more information about the surface symmetry, SH signals will need to be taken as the sample is rotated about the surface normal. Experiments involving circularly polarized light can also help to resolve the nonvanishing tensor elements.

4.2.2 Observation of Photodynamics of Oxygen on Rutile Surface

When comparing the signal levels in Fig. 4.6 and Fig. 4.7, the s-total was higher in the oxygen environment while the p-total was slightly smaller in oxygen than in the vacuum. The p-total signal rose from a lower level as the laser fluence upon the sample surface in the vacuum increased. The lower signal was recovered by keeping the sample in the vacuum (O_2 partial pressure 10^{-10} torr) for several days or flushing the chamber with a few torr of oxygen. Oxygen gas was introduced into the chamber through a long stainless steel coil which was cooled to 77 K to remove water vapor. In Fig. 4.8, a high SH signal in the beginning was the result of previous exposure of the sample to the green

Symmetry classes	SH components	Nonvanishing tensor elements
$C_{4\nu}$ or $C_{6\nu}$	pp: a, b, c	a=zzz, b=zxx=zyy, c=xxz=xzx=yzy=yyz
mirror planes	ps: none	
in x-z and y-z	sp: b	
	ss: none	
C_4 or C_6	pp: a, b, c	a=zzz, b=zxx=zyy, c=xxz=xzx=yzy=yyz
no mirror	ps: d	d=xyz=xzy=-yxz=-yzx
	sp: b	
	ss: none	
C_{3v}	pp: a, b, c	a=zzz, b=zxx=zvy, c=xxz=xzx=vzy=vyz
mirror plane	ps: d	d=yyy=-yxx=-xxy=-xyx
in y-z	sp: b	
	ss: d	
C ₃	pp: a, b, c, e	a=zzz, b=zxx=zyy, c=xxz=xzx=yzy=yyz
no mirror	ps: d, f	d=yyy=-yxx=-xxy=-xyx, e=xxx=-xyy=-yyx=-yxy
	sp: b, e	f=xyz=xzy=-yzz=-yzx
	ss: d	
$C_{2\nu}$	pp: a, b, d	a=zzz, b=zxx, c=zyy, d=xxz=xzx, e=yzy=yyz
mirror planes	ps: none	
in x-z and y-z	sp: c	
	ss: none	
C ₂	pp: a, b, d	a=zzz, b=zxx, c=zyy, d=xxz=xzx, yzy=yyz
no mirror	ps: e	<i>zxy=zyx</i> , e= <i>yxz=yzx</i> , <i>xyz=xzy</i>
	sp: c	
	ss: none	
$C_{i\nu}$	pp: a, b, d	a=zzz, b=zxx, c=zyy, d=xxz=xzx, yzy=yyz
mirror plane	ps: f, g	<i>zzy=zyz</i> , <i>xxy=xyx</i> , e= <i>yyy</i> , f= <i>yxx</i> , g= <i>yzz</i>
in y-z	sp: c	
	ss: e	
$C_{1\nu}$	pp: a, b, d, e, g, h	a=zzz, b=zxx, c=zyy, d=xxz=xzx, yzy=yyz
mirror plane	ps: none	e=xxx, f=xyy, g=xzz, h=zzx=zxz, yyx=yxy
in x-z	sp: c, f	
	ss: none	

Table 4.1: Nonvanishing elements of $\chi^{(2)}(2\omega;\omega,\omega)$ and their contributions to the polarization dependent SH signals for surfaces of various symmetry classes. The first rank is that of the output photon. The surface is in the x-y plane and x-z is the scattering plane.



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Fig. 4.6 Polarization components of the SH signal of rutile in vacuum. KG-4 color glass filter was to block UV and establish the base line of the signal level.



Fig. 4.7 Polarization components of the SH signal of rutile in an oxygen environment.

for a very long period of time. The signal dropped promptly upon the introduction of oxygen. Following the evacuation of oxygen, the p-total signal increased slowly. The signal to noise ratio was higher in the second part of the data set only because 8,000 shots were averaged per data point while 4,000 shots were used for the first part. The reflectivity of the sample remained constant through the experimental period regardless of the conditions. This would rule out the possibility that heating of bulk rutile contributed to the changes in SSHG.

We also have concluded that the changes of SH signal in the vacuum environment were photo-initiated while the changes observed in the oxygen environment were not caused by light. The results shown in Fig. 4.9 support these notions. After introducing oxygen into the vacuum chamber, the green laser probed the sample surface for only several seconds or a few minutes. The upper curve showed the decreasing ptotal and the lower curve the rising s-total. When the oxygen was pumped out of the chamber, the s-total decreased only during the period when the laser beam was applied.

To confirm that oxygen was the only cause of the changes on the rutile surface, nitrogen gas was introduced into the chamber. When flowing nitrogen into the chamber from a commercial cylinder, in addition to the stainless steel coil in a liquid nitrogen cold trap (to remove water), a reduced copper gas purifier was inserted before the trap to remove oxygen. The gas purifier consisted of a 4-meters long 1/4-inch copper tubing. When heated up to 250°C, it could remove the oxygen contamination from the nitrogen flow as copper(II) oxide (CuO). To prepare the coil for another experiment hydrogen gas reduced CuO formed in the inner surface of the tubing back to copper at 250°C. Any hydrogen in the nitrogen stream was also removed by reaction with CuO to form H₂O and subsequent trapping of water in the liquid nitrogen trap. It appeared that nitrogen has no effect on the SSHG signal.

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Fig. 4.8 SH signal (p-total) of rutile responded to the presence of oxygen while the reflectance remained unchanged.



Fig. 4.9 The changes in the SH signal of rutile as the environment changed. The changes in the oxygen environment were light-independent. It happened as soon as oxygen was admitted into the chamber. The changes in the vacuum, on the other hand, were photo-initiated. When the light was blocked, the signal level remained the same.

These results could be interpreted as adsorption of O_2 onto Ti³⁺ surface defect sites to create Ti⁴⁺: O_2^- species and the photo-desorption of O_2 from these sites. Gopel *et al.*³⁹ reported that oxygen vacancies were produced on the TiO₂ (110) surface after the sample was heated up to 600°C in vacuum and that O_2 molecules interacted with the vacancies to produce chemisorbed O_2^- species. Yanagisawa and Ota⁴⁰ studied the photodesorption of chemisorbed O_2^- from powder TiO₂ surfaces and found that by UV illumination with an energy above 3.0 eV photo-stimulated-desorption of O_2 occurs at room temperature. In a continuation of our study, Jang used UV 266 nm (4.7 eV) as the excitation energy source and observed the same magnitude of changes in the SH signals with a fluence of UV 10⁴ times less than that of the green.⁴¹ It is still not clear whether the desorption of O_2^- is caused by one photon absorption of O_2^- itself at 266 nm, or by the electron-hole pair generation of rutile in the subsurface region upon above band gap irradiation as the photo-generated holes migrate to the surface and recombine with the chemisorbed O_2^- to form physisorbed O_2 which desorbs thermally at room temperature. The second model was proposed by Yanagisawa and Ota.⁴⁰

4.2.3 Photo-desorption of Oxygen by Green Excitation

The surface adsorption of O_2 and the consequent oxidation of Ti³⁺ is a reasonable explanation for the light-independent variation of SH signals in the oxygen environment. Jang also found that the oxidation rate (by monitoring the SH signal) was proportional to the collision rate of O_2 on the photoreduced rutile surface to the power of approximately 0.2. However, the desorption of O_2^- with green 532 nm excitation is quite puzzling. The photon energy of green light is below the rutile band gap, and the O_2^- molecule does not absorb it either. Two possible mechanisms were rejected based upon the following estimations. (1) Two photon absorption by either O_2^- or rutile:

Take a typical two photon absorption cross section $\sigma \approx 10^{-51}$ cm⁴ sec and 50 mW of green focused down to a spot of 100 µm in diameter, which provides $I_{\omega} \approx 1.3 \times 10^{21}$ photons/(cm² sec). The rate constant of this process is $\frac{1}{N} \frac{dN}{dt} = \sigma I_{\omega}^{-2} \approx 1.7 \times 10^{-9}$ sec⁻¹, and this means that it will take more than 15 years to ionize a monolayer of O₂⁻.

(2) One photon excitation with UV from SSHG of rutile:

We have estimated the typical SH conversion efficiency in our experiment to be 10^{-12} (section 4.1.2), which fell well too short of the observed 10^{-4} ratio, when directly using UV as excitation, as reported by Jang (section 4.2.2).

Assume that the rutile sample has a surface density $N_4 ~(\approx 10^{15} \text{ cm}^{-2})$ for Ti⁴⁺ and $N_3 ~(\approx 10^{13} \text{ cm}^{-2})$ for the Ti³⁺ defects. If the photoreduction process is dependent upon I_{ω} to the n-th power, then the reduced defect density is $N_{\text{re}} = N_3 (1 - e^{-\eta t})$ and the oxidized defect density is $N_{\text{ox}} = N_3 e^{-\eta t}$, with the rate constant $\eta \propto I_{\omega}^{\text{n}}$. The normalized SH signal should be

$$I_{2\omega}(t) \propto |N_4\beta_4 + N_{\rm re}\beta_{\rm re} + N_{\rm ox}\beta_{\rm ox}|^2 = |N_4\beta_4 + N_3\beta_{\rm re} + N_3(\beta_{\rm ox}-\beta_{\rm re})e^{-\eta t/2}, \tag{4.1}$$

where β_4 , β_r and β_{ox} are the microscopic second order susceptibilities. In Fig. 4.10 to Fig. 4.14, Eq.(4.1) was fitted into five data sets with average green power between 56 and 24 mW. Given the noise level in the data, the resulting rate constants, about $(4\pm1)\times10^{-4}$ sec⁻¹, were not sensitive to the input green power. For all five data sets with s-total signals, the chamber was flushed with oxygen, up to a few torr, to fully oxidize the sample and then pumped down to 10^{-6} torr total pressure before the green was allowed to hit the sample. Beside the long time decay constant $\eta = (4\pm1)\times10^{-4}$ sec⁻¹, there was a quick drop in the first few minutes after the laser struck. The rate constants were an order of magnitude greater than the long time ones, but it was also difficult to tell whether there was a power dependence in these short decay constants or not.



Fig. 4.10 Photoreduction rate of the rutile surface in vacuum at 56 mW of laser power. The curves were simulations of Eq.(4.1).



Fig. 4.11 Photoreduction rate of the rutile surface in vacuum at 48 mW of laser power. $\eta = 0.0004$ sec⁻¹ was the best fit.



Fig. 4.12 Photoreduction rate of the rutile surface in vacuum at 40 mW of laser power.



Fig. 4.13 Photoreduction rate of the rutile surface in vacuum at 35 mW of laser power.



Fig. 4.14 Photoreduction rate of the rutile surface in vacuum at 24 mW of laser power.



Fig. 4.15 SSHG observation of the adsorption and desorption of water molecules on the rutile surface. The water vapor was less than 1 torr in the chamber.

In Fig. 4.14 with input power of 24 mW, the quick drop in the early minutes was less obvious and might be just buried in the noise because of the smaller signal-to-noise ratio.

As we have varied the input power by more than a factor of two, the rate constant, with the big uncertainty, only reflects a power dependence $\eta \propto I_{\omega}^{n}$ with n < 1 or n ≈ 0 . This indicates a possible saturated mechanism in the 532 nm photoreduction process. That is, either the defects responsible of photon absorption are easily saturated or there is a recombination or relaxation mechanism which depends upon the excitation density. While the SSHG does provide the surface sensitive observations, the definitive interpretation of the photoreduction observations will require further investigation combined with other experimental techniques.

On a photoreduced rutile surface, the adsorption and desorption of water molecules were also observed by monitoring the p-total signal (Fig. 4.15) as less than 1 torr of water vapor was admitted into the chamber and pumped out later. The rising signal of the beginning of this data set was due to the continuation of the photoreduction process in vacuum. The photodesorption of adsorbed water is apparent. When a half reduced surface was exposed to hydrogen gas, a slight increase in the photoreduction rate was observed. No significant change in the SH signal and the polarization ratios was found when a fully reduced surface was exposed to 1 torr of H₂. So we conclude that hydrogen can not further reduce or reoxidize the surface at room temperature, although it is capable of reducing the rutile at high temperature.

4.2.4 Conclusion

We have demonstrated that SSHG is capable of providing surface information about rutile, although the bulk medium also contributes to the signal, *e.g.* the nonzero ps and ss components. Surface adsorption and desorption of water and oxygen molecules have been observed by SSHG. This study also led to the observation of photo-induced reduction of the rutile surface in vacuum with laser pulses at 532 nm. Interpretation of this phenomenon consists of a model in which oxygen molecule, initially bound strongly as O_2^- , desorbs, leaving behind Ti³⁺ surface defects. These defects readily bind O_2^- quickly at a pressure above 10^{-5} torr. The propensity of the surface to undergo photoreduction correlates with a decreasing photo-ablation threshold. The damage thresholds are 490 and 650 MW/cm² in vacuum and 1 torr of O_2 , respectively. The surface photoreduction rate is insensitive to the applied laser power in the range which provides measurable SH signals.

4.3 Amorphous Carbon Films

Recently, amorphous hydrogenated carbon (*a*-C:H) films have been used in the applications of optical coatings, protective coatings, semiconducting devices *etc.* as well as having been studied as candidates for electroluminescence materials.⁴² Their versatile properties include extreme hardness, optical transparency in the visible and near infrared regions, chemical inertness and low coefficient of friction. The most common methods of deposition are rf-biased (dc bias voltage > 100 V) plasma deposition from a hydrocarbon gas (*a*-C:H), direct low-energy (30-100 eV) ion beam deposition (*i*-C for ion beam deposited carbon or DLC for diamond-like carbon), dc glow-discharge decomposition of hydrocarbon gas deposition, and by variations of sputtering processes. The properties of carbon films are independent of their hydrocarbon sources, and methane (CH₄) and benzene (C₆H₆) are among those mostly used. On the other hand, the film properties can vary substantially according to the deposition parameters such as bias voltage, rf power density, substrate temperature, pressure (< 0.1 torr) and composition ratio of hydrocarbon gas and carrier gas (usually argon, nitrogen or hydrogen), and the post heat treatment.

Characterization of *a*-C:H films has been pursued with all kinds of experimental techniques. Collins⁴³ has used in situ ellipsometry to perform real time measurements of index of refraction and extinction coefficient during the thin-film growth. Grundy et al.⁴⁴ have measured the composition of the film, especially the hydrogen content, by glancing angle neutron scattering. It is known that a-C:H consists of a mixture of sp^2 and sp^3 hybridized carbon atoms, some of which are bonded to hydrogen. It has also been shown⁴⁵ that, for plasma-deposited films, as the hydrogen content decreases, the mass density, hardness and sp^2/sp^3 ratio increase. The hydrogen content and the sp^2/sp^3 ratio were the subjects of solid state proton and carbon-13 NMR studies by Bustillo et al.46 The infrared spectrum of the C-H stretching mode is also a good measure of hydrogen content.^{47,48} When plasma-deposited *a*-C:H is thermally annealed at 600°C, hydrogen can effuse out of the films⁴⁷ which contain now only *sp*² bonded carbon,⁴⁹ and crystallization into the graphite phase takes place. The typical microcrystallite size is 30 to 50 A (Angstroms) along the graphite planes, as measured by Raman spectroscopy, and less than 10 A in the direction perpendicular to the basal planes according to x-ray diffraction measurements.⁴⁷ Reyes-Mena et al.⁵⁰ have observed light-induced changes in the photoluminescence spectrum of *a*-C:H at low temperature, with a recovery temperature around 200 K which is in contrast to 150° C for amorphous silicon (a-Si:H).

There are two Raman-active modes of all *a*-C:H samples.^{47,51} The G band (G as graphitic) is found between 1530 and 1580 cm⁻¹, and the D band (D as disordered) around 1350 cm⁻¹. The Raman spectrum of a single crystal of graphite reveals only the G band, while the D band appears only where the graphite crystallites are reduced to domains of finite size (tens Angstroms). Since the D band is ascribed to the presence of disordered *sp*² carbons, some researchers consider the relative Raman intensity of the D and G bands as a measure of the degree of order in an *a*-C:H sample while others disagree.⁵² With increasing exciting photon energy, a high-frequency shift of the G band

has been observed by resonant Raman scattering.^{53,54} This shift is interpreted in terms of scattering from π -bonded (sp^2) carbon clusters which is resonantly enhanced for incident photon energies approaching the π - π^* resonance. This interpretation provides support to theoretical models⁵⁵ saying that hard *a*-C:H films consist of sp^2 carbon clusters interconnected by sp^3 sites.

Diamond thin films have been grown in high frequency (microwave) plasma CVD (chemical vapor deposition) or hot filament (over 2000°C) CVD chambers on substrates at 1000°C with gas mixtures (0.5-50 torr) containing less than 0.5% CH₄ in H₂.⁵⁶ The crystalline diamond has been identified by x-ray/electron diffraction and Raman spectrum which has a characteristic peak at 1332±1 cm⁻¹ for diamond. Nitrogen-doped *a*-C:H films deposited with carrier gas consisting of a variable ratio of N₂-Ar mixture have also been studied, and the nitrogen incorporated can be as much as 20%.⁵¹

With the film's extreme hardness and chemical inertness in mind, second harmonic generation was considered to study the surface properties and any possible surface modification of *a*-C:H under various conditions. The *a*-C:H films were deposited on one inch in diameter quartz substrates which has negligible contribution to SH signal. The deposition detail has been described in reference 51. The thin film was estimated to be about 250 Angstroms thick based upon an ellipsometric measurement.

4.3.1 Low Laser Power Study

We started with an average of 6 mW of green (532 nm) in a 3 mm diameter beam on the sample under a vacuum at 2×10^{-8} torr. The power density within the laser pulse was about 57 KW/cm². While there was no observable SH signal from the sample at this low power density level, reversible light-induced intensity decay in photoluminescence (PL) was observed (Fig. 4.16). PL was collected through a focal



Fig. 4.16 The intensity decay of photoluminescence of a-C:H excited by less than 60 KW/cm² green pulses. There was a 12 hour time span between (a) and (b) without laser irradiation, during which the PL recovered at room temperature.

lens set up 45° away from the reflected green and sent through several sharp cut orange glass (Schott, OG-550 and OG-570) filters to eliminate scattered green before detection by a PMT (Fig. 4.1). The recovery time of PL was between a few hours to 12 hours at room temperature in vacuum (2×10^{-8} torr). Reyes-Mena *et al.*⁵⁰ first reported this light-induced fatigue of PL in both the spectra and the integrated intensity in the *a*-C:H films, and more significant changes were observed at temperatures between 13 K and 200 K. Although light-induced metastable changes in the properties of amorphous materials have been observed for some time, especially of amorphous hydrogenated silicon (*a*-Si:H), there is still a lack of basic understanding of the nature of the microscopic mechanism responsible for those observations. Some proposed models ascribe these fatigue effects to the enhancement of the nonradiative recombination by the creation of dangling bonds due to intense illumination.

4.3.2 Medium Laser Power Study

As the laser power was increased to 80 mW and loosely focused down to 0.5 mm in diameter, the average pulse power density was about 27 MW/cm² or 2.7 mJ/cm² in a 100 ps pulse. At this medium power level, the intensity of PL dropped faster (Fig. 4.17) than at the low power level and only recovered partially after a long break. When methanol vapor was introduced into the vacuum chamber, PL signal level rose substantially. The signal dropped back slowly as the vapor was pumped out of the chamber. Water vapor was found to have a similar effect on the *a*-C:H sample. The PL signal was lower when air was brought into the chamber, probably due to oxygen, and slowly recovered in vacuum. In Fig. 4.18 we plot the PL signal against laser power density in three different enviroments. After the initial annealing as shown in Fig. 4.17, the properties of the thin film became stabilized when it responded to laser pulses of this



Fig. 4.17 The intensity decay of photoluminescence of a-C:H excited by 27 MW/cm² green pulses. The two lower signal levels were checked with lower power densities, 45% and 12% respectively.



Fig. 4.18 Photoluminescence of *a*-C:H film in various environments. (a) In vacuum $(2 \times 10^{-8} \text{ torr})$, (b) in several millitorr of air, and (c) in several millitorr of methanol vapor.

medium power density level, and the PL changes upon exposure to methanol, water and air were all reversible.

There was no observable SH signal of *a*-C:H film under atmospheric conditions at this laser power density. In Fig. 4.19, SH (p-total) and green reflectance of the thin film were monitored simultaneously in vacuum. Each data point represented the response to a single laser Q-switch pulse train which ran at a 500 Hz repetition rate. The whole data set thus only took a little more than 2 seconds. Both graph (a) and graph (b) show the results from new spots on the sample. A shutter blocking the incident laser beam released after the first few data points and caused the low signal level at those points. Graph (b) was taken with an additional KG-4 glass filter, which transmits green and blocks UV, in the path of SH signal before it reached PMT. The low signal counts of graph (b) in SH channel demonstrated that the corresponding signal of graph (a) was UV at 266 nm. Both SH signal level and reflectance dropped slightly upon irradiation, which indicated that the *a*-C:H film was quickly modified by either intense illumination or thermal heating. After that quick drop, both signal levels remained stable. Although the initial higher signal levels did not recover even after the incident laser beam was blocked for 20 minutes.

The SH signal, unlike the PL signal, decreased as methanol vapor was introduced into the vacuum chamber and rose back when the vapor was pumped out. The effect of methanol was plotted in Fig. 4.20, where each data point was averaged over 1000 laser shots (Q-switch pulse trains).

4.3.3 High Laser Power Study

When the laser beam was focused down to 0.1 mm in diameter, with average laser power of 160 to 200 mW, we were able to apply more than 1.5 GW/cm² to the thin film sample. The result is shown in Fig. 4.21. The SH signal started with a big spike


(a)



Fig. 4.19 SH signal and green reflectance of *a*-C:H film at new sample spots in vacuum. Average laser pulse power density was 27 MW/cm². Each data point corresponded to a single laser Q-swith pulse train. Graph (b) was taken with an additional KG-4 filter in the SH signal path to demonstrate that the signal in graph (a) was UV.



Fig. 4.20 SH signal of *a*-C:H film was lower in the presence of several millitorr of methanol vapor. Each data point averaged over 1000 laser shots. The average laser pulse power density was 27 MW/cm².

and then settled down quickly while both PL and reflectance of the film dropped more slowly and smoothly. Under the microscope, the transparent *a*-C:H film was turned into a transparent, dark spot of 100 μ m wide and 200 Angstrom deep. The depth of the hole was measured by an Alpha-step 100 profilometer. The composition of the dark ultra-thin film remaining in the bottom and the edge of the hole is unknown. It can be easily scratched off by a stainless-steel tweezer, so it is not as hard as the original *a*-C:H film. Under atmospheric conditions the *a*-C:H film was totally ablated by laser pulses at 300 MW/cm², clear substrate being left behind.

Since the residual thin film is soft and dark, it might be related to graphite. But it is doubtful that graphite film, which has zero optical bandgap, could endure such intense laser pulse better than the a-C:H film did. This ultra-thin dark film is still photo-active in various gaseous environments. It was indefinitely stable in the vacuum environment and the p-total and s-total SH signals were about equal. Both ps (p-in, s-out) and ss (s-in, sout) components were below the noise level. As soon as oxygen was introduced into the chamber, the SH signal dropped substantially and the film was ablated completely. With 80 millitorr of methanol vapor, the SH signal rose slowly by 10 to 20% over a few hours before levelling off. With 0.3 torr of nitrogen (standard grade, 1 ppm of moisture and 5 ppm of oxygen), the SH signal rose, also slowly, as much as 50% in five and a half hours. A similar effect was observed when we turned the ion pump off and let the vacuum chamber out-gas long enough. The major out-gasing species were detected by a RGA (residual gas analyzer, Ametek, MA100). Five hours after the pump was turned off, total pressure in the chamber rose from 2×10^{-8} torr to 3×10^{-5} torr. The species of highest partial pressure were hydrogen $(1 \times 10^{-5} \text{ torr})$ and nitrogen $(2 \times 10^{-6} \text{ torr})$. Species of atomic mass unit 14 (N or CH₂), 15 (NH or CH₃), 16 (NH₂, CH₄ or O) also had higher partial pressure at 3×10^{-7} , 1×10^{-6} and 1×10^{-6} torr and those were indicative of fragments of several hydrocarbons. Water was less than 1×10^{-8} torr. Both oxygen and



Fig. 4.21 SH, PL and green reflectance of a-C:H film under more than 1.5 GW/cm² laser pulses. Each data point averaged over 1500 laser shots, which took approximately 3 seconds. The SH signal started with a big spike and settled down quickly while the film was ablated and left with an ultra-thin film of unknown composition.



Fig. 4.22 All signals from the residual dark film rose after the vacuum chamber out-gassed for 3 days. Laser pulse power density was about 1.5 GW/cm². The total pressure in the chamber was less one millitorr. All the signals rose from the same level as 3 days before. Each data point averaged over 1500 laser shots.

methanol were below 1×10^{-9} torr. The observed increases in SH were all photo-induced processes. An example is given in Fig. 4.22, where the SH signal went up after the pump was off for 3 days, and the initial signal level was the same as that obtained previously. The changes in SH, also accompanied by changes in PL and sample reflectance, were irreversible. When the chamber was pumped down again, the SH dropped but never went back to the level it was before. This showed that the properties of the residual dark thin film were continually altered by the intense laser pulses in the gaseous environments.

4.3.4 Laser Heating

Since the heat treatment of *a*-C:H film can change its hydrogen content and sp^2/sp^3 bonding ratio and, hence, the film's properties, laser heating could have played a major role in the reversible, and irreversible phenomena and the photo-ablation process we encountered. Electrons in the material are first excited upon absorption of laser light. This electronic excitation couples to the vibrational modes in 10^{-12} sec.⁵⁷ and diffuses away. The temperature rise at any time is proportional to the total energy deposited in the material and can be calculated from the heat conduction equation and the thermal properties of the thin film and the substrate. The optical density of our *a*-C:H sample was 0.13 (*i.e.* about 74% transmission) at 532 nm measured by a UV/Visible spectrophotometer (Perkin-Elmer Lambda 3B). The optical density of the quartz substrate was on the order of 10^{-4} .

The heat conduction or Laplace diffusion equation is

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} = \frac{1}{\kappa} \frac{\partial T}{\partial t},$$
(4.2)

where $\kappa = \frac{K}{\rho c}$ is the thermal diffusivity (cm²/s). *K*, ρ and *c* are the thermal conductivity

(Watt/cm K), density (g/cm³) and specific heat (J/g K). Carslaw and Jaeger⁵⁸ have presented general solutions to heat conduction problems for a variety of geometries. For an instantaneous point heat source at (x', y', z') which liberates a total energy of Q, the solution to Eq.(4.2) of any point (x, y, z) in the medium at time *t* after is

$$\Delta T = (Q / \rho c) (4\pi\kappa t)^{-3/2} \exp\{-[(x - x')^2 + (y - y')^2 + (z - z')^2] / (4\kappa t)\}.$$
(4.3)

If the heat source is on the surface of a semi-infinite medium, that is z' = 0 and vacuum in z < 0, then ΔT is twice that expressed in Eq.(4.3) because heat only diffuses into the space of z > 0.

To describe the effect of a pulse of Gaussian transverse profile, we need to begin with the problem of a heat source in the shape of a ring. Considering the instantaneous heat source to be a uniform ring on the surface with the total energy Q, ΔT in cylindrical coordinates becomes

$$\Delta T = \frac{2}{(4\pi\kappa t)^{3/2}} \int_0^{2\pi} \frac{Q}{\rho c 2\pi r'} \exp[-\frac{z^2 + r^2 + r'^2 - 2rr'\cos(\theta - \theta')}{4\kappa t}]r' d\theta'$$

where $r^2 = x^2 + y^2$ and θ can be arbitrarily set to zero for the isotropic medium. $r'^2 = x'^2 + y'^2$ is the radius of the source ring. After we rearrange the expression into

$$\Delta T = \frac{Q}{\rho c (4\pi\kappa t)^{3/2}} \exp(-\frac{z^2 + r^2 + {r'}^2}{4\kappa t}) \frac{1}{\pi} \int_0^{2\pi} \exp(\frac{2rr'\cos\theta'}{4\kappa t}) d\theta',$$

the integral can be expressed by the modified Bessel function

$$I_0(\omega) = (1/\pi) \int_0^{\pi} \exp(\pm \omega \cos \theta') d\theta',$$

and we have

$$\Delta T_{\text{ring source}} = \frac{2Q}{\rho c (4\pi \kappa t)^{3/2}} \exp(-\frac{z^2 + r^2 + r'^2}{4\kappa t}) I_0(\frac{rr'}{2\kappa t}).$$
(4.4)

Eq.(4.4) can be integrated over r' to obtain the result for a surface heat source with transverse Gaussian profile. If the Gaussian radius is $r_{\rm G}$ the total energy becomes

$$Q = \int_0^\infty Q_0 \exp(-r'^2 / r_G^2) 2\pi r' dr' = \pi r_G^2 Q_0,$$

and the temperature rise in an isotropic semi-infinite solid is

$$\Delta T_{\text{Gauss}} = \frac{2Q_0}{\rho c (4\pi\kappa t)^{3/2}} \exp(-\frac{z^2 + r^2}{4\kappa t}) \int_0^\infty \exp(-\frac{r'^2}{4\kappa t} - \frac{r'^2}{r_G^2}) I_0(\frac{rr'}{2\kappa t}) 2\pi r' dr'$$
$$= \frac{2\pi Q_0}{\rho c (4\pi\kappa t)^{3/2}} \exp(-\frac{z^2 + r^2}{4\kappa t}) \int_0^\infty \exp[-x(\frac{1}{4\kappa t} + \frac{1}{r_G^2})] I_0(\frac{r\sqrt{x}}{2\kappa t}) dx.$$

The last integral can be evaluated through the Laplace transform of the modified Bessel function. Upon applying the integral identity

$$\int_0^\infty \exp(-bx) I_0 \left(2a\sqrt{x}\right) dx = \frac{\exp(a^2/b)}{b}$$

we reach the result

$$\Delta T_{\text{Gauss}} = \frac{2\pi Q_0}{\rho c (4\pi\kappa t)^{3/2}} \exp(-\frac{z^2 + r^2}{4\kappa t}) \frac{4\kappa t r_G^2}{4\kappa t + r_G^2} \exp[\frac{r^2}{(4\kappa t)^2} \frac{4\kappa t r_G^2}{4\kappa t + r_G^2}]$$
$$= \frac{\pi r_G^2 Q_0}{\rho c \pi^{3/2} (\kappa t)^{1/2}} \frac{\exp(-z^2 / 4\kappa t)}{4\kappa t + r_G^2} \exp[-\frac{r^2}{4\kappa t} + \frac{r^2 r_G^2}{4\kappa t (4\kappa t + r_G^2)}]$$
$$= \frac{Q}{\rho c \pi^{3/2} (\kappa t)^{1/2}} \frac{\exp(-z^2 / 4\kappa t)}{4\kappa t + r_G^2} \exp(-\frac{r^2}{4\kappa t + r_G^2}). \tag{4.5}$$

The heat converted from the laser pulse diffuses a distance on the order of $(\kappa t)^{1/2}$ into the medium. The temperature rise at any time is proportional to the total energy deposited in the medium over this thermal diffusion length. The specific heat (*c*) and thermal conductivity (*K*) are temperature dependent, and so is the thermal diffusivity (κ). For material like graphite, the thermal diffusion length is no more than 0.5 µm during the 100 ps laser pulse. It is less than 20 nm for the quartz substrate. We thus consider each 100 ps laser pulse as an instantaneous heat source, with a transverse Gaussian profile of 0.1 to 3 mm in diameter, in the thin film and the substrate within the thermal diffusion length. The energy is converted only from the absorption of the thin film (about 25 nm). The calculation of the temperature rise takes into account the energy contribution from every laser pulse in a Q-switch pulse train as the initial temperature at each pulse keeps changing. To estimate the temperature of the thin film instead of the substrate, the result

of Eq.(4.5) has to be modified for the anisotropic case, that is $\kappa_x = \kappa_y = \kappa \neq \kappa_z$. κ_z is the thermal diffusivity of the quartz substrate and κ is that of *a*-C:H thin film. The heat conduction equation in Eq.(4.2) is rewritten as

$$\kappa \frac{\partial^2 T}{\partial x^2} + \kappa \frac{\partial^2 T}{\partial y^2} + \kappa_z \frac{\partial^2 T}{\partial z^2} = \frac{\partial T}{\partial t}.$$

The solution for a surface ring heat source of Eq.(4.4) becomes

$$\Delta T_{\text{ring source}} = \frac{2Q}{\rho c (4\pi\kappa t) (4\pi\kappa_z t)^{1/2}} \exp(-\frac{z^2}{4\kappa_z t}) \exp(-\frac{r^2 + r'^2}{4\kappa t}) I_0(\frac{rr'}{2\kappa t})$$

Finally the result of a surface heat source with a transverse Gaussian profile is

$$\Delta T_{\text{Gauss}} = \frac{Q}{\pi^{3/2} [(\rho c)_{\text{substrate}} (\kappa_z t)^{1/2} + (\rho c)_{\text{film}} d]} \frac{\exp(-z^2 / 4\kappa_z t)}{4\kappa t + r_G^2} \exp(-\frac{r^2}{4\kappa t + r_G^2}). \quad (4.6)$$

In the last equation, the heat capacity of the thin film is taken into account as well as that of the quartz substrate. d is the thickness of the film.

The density, specific heat and thermal conductivity of *a*-C:H as a function of temperature are not available, so the data for graphite are used for the estimation. The average thermal conductivities in the directions parallel and perpendicular to the layer planes of graphite are adopted for the amorphous thin film. The temperature dependent thermophysical data⁵⁹ for the film and the substrate are fitted to polynomials between 200 and 4000 K for the calculation. Notice that the sublimation point of graphite is 3925 K and the melting point of fused quartz is 1883 K. The computer program written in Quick Basic to estimate the sample temperature according to Eq.(4.6) under various laser pulse power densities is listed in Appendix C. We plot the typical results of the calculation in Fig. 4.23. After each Q-switched pulse train (400 nanoseconds), the sample temperature declines to the initial level before the next pulse train strikes, which is 2 milliseconds later. While within a pulse train, energies are accumulated from every mode-locked pulse (0.1 ns in duration) prior to the temperature evaluation. There are 10 ns between the ML pulses, and the temperature (evaluated every 0.5 ns) drops



Fig. 4.23 Estimated temperature rise of 250 A *a*-C:H film heated by a laser pulse train with an average pulse intensity of 1.5 GW/cm². The calculated position is around the beam. The Q-switched pulse train is 400 ns in duration and there are 10 ns between mode-locked pulses. The temperature is calculated every 0.5 ns inside the pulse train. (a) Temperature drops back to the initial level before the next pulse train (2 ms later) arrives. (b) First 1 μ s of the temperature response is plotted. Each ML pulse intensity is according to a simulation of the envelope of a pulse train.

substantially between pulses. The envelope of the transient temperature spikes following each ML pulse is due to the simulation of the pulse intensity of a Q-switched pulse train. These spikes, as the matter of the choice of the time period Δt , provide the upper boundaries of the estimated temperatures. The more realistic maximum temperature is that below those spikes.

Under high intensity (about 1.5 GW/cm²) which could blow off most of the *a*-C:H film, the maximum transient temperature following the short laser pulse is estimated 1747 K around the laser beam (Fig. 4.23) and above 4000 K at the center of the beam. According to Angus *et al.*⁶⁰ *a*-C:H film turns to graphite when it is annealed between 900 and 1300 K. But whether our short heat pulses produce the same effect on the *a*-C:H film as the long time annealing process does is not clear. At medium intensity (about 27 MW/cm²) which is below the damage threshold, the maximum transient temperature at the center of laser beam is no more than 550 K. With low intensity (about 57 KW/cm²), for which only recoverable PL fatigue was observed, the temperature spikes are less than 0.5 degree above initial temperatue which indicates no laser heating.

4.3.5 Conclusion

The transparent, hard, low-friction *a*-C:H films are photo-active under a wide range of laser pulse intensities. Using second harmonic generation to study the surface of the films was unsuccessful because we could not have measurable SH signals without modifying the films. Even for a weak laser intensity, at which there was no laser heating estimated, the film responded with changes in the photoluminescence intensity and took several hours to recover at room temperature. With the power density below the damage threshold, the temperature of the film could be raised by several hundred degrees, and the film was irreversibly modified as observed by the PL and the SH. In the presence of methanol vapor, we also observed that the PL signal went up while the SH down. The presence of oxygen lowered the damage threshold to an approximately 300 MW/cm², and the film was ablated without residue.

In vacuum, photo-ablation of the film occured when the power density exceeded 1 GW/cm². A dark, soft material was left behind. This residual material was still photoactive when exposed to various gases, such as hydrogen, nitrogen, oxygen or methanol vapor. At this intensity level, the temperature of the film was estimated to be as high as one thousand degrees during the laser pulse train. It quickly cooled down between pulse trains because of the good thermal conductivity of the film.

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61. This integral identity was originally derived by P. P. Ewald (reference 2). The proof we show here is that of Dr. Fuxiang Han (private communication).

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APPENDICES

Appendix A. Integral Identities for Planewise Lattice Sum

A-1:
$$\frac{e^{ikr}}{r} = \frac{2}{\sqrt{\pi}} \int_{(0)}^{\infty} \exp\left(-r^2 t^2 + \frac{k^2}{4t^2}\right) dt .61$$

First of all, change the variable in the integral to $t^2 = x$, then $dt = \frac{dx}{2\sqrt{x}}$.

rhs =
$$\frac{2}{\sqrt{\pi}} \frac{1}{2} \int_{(0)}^{\infty} x^{-\frac{1}{2}} \exp\left(-r^2 x + \frac{k^2}{4x}\right) dx = \frac{1}{\sqrt{\pi}} \int_{(0)}^{\infty} x^{-\frac{1}{2}} \exp\left[-\frac{kr}{2}\left(\frac{2r}{k}x - \frac{k}{2rx}\right)\right] dx.$$

Using $y = \frac{2r}{k}x$, rhs $= \frac{1}{\sqrt{\pi}} \left(\frac{k}{2r}\right)^{\frac{1}{2}} \int_{0}^{\infty} y^{-\frac{1}{2}} \exp\left[-\frac{kr}{2}\left(y-\frac{1}{y}\right)\right] dy$. Do it again with y = -iz

and dy = -*i*dz, then rhs = $\left(\frac{k}{2\pi r}\right)^{\frac{1}{2}}(-i)(-i)^{-\frac{1}{2}}\int_{0}^{i\infty} z^{-\frac{1}{2}} \exp\left[i\frac{kr}{2}\left(z+\frac{1}{z}\right)\right] dz$. In the last

integral, $0 = \oint = \int_{(0)}^{i\infty} + \int_{i\infty}^{\infty+i\infty} + \int_{\infty+i\infty}^{\infty} + \int_{\infty}^{(0)}$, but the two integrals in the middle are

zero due to $z^{-\frac{1}{2}}$, so the expression is left with

rhs =
$$\left(\frac{k}{2\pi r}\right)^{\frac{1}{2}}(-i)(-i)^{-\frac{1}{2}}\int_{0}^{\infty}z^{-\left(-\frac{1}{2}\right)-1}\exp\left[i\frac{kr}{2}\left(z+\frac{1}{z}\right)\right]dz$$
. Now, by comparing this with

an integral identity of the Hankel function of first kind,

$$H_{\nu}^{(1)}(x) = -\frac{i}{\pi} e^{-\frac{1}{2}i\nu\pi} \int_{(0)}^{\infty} t^{-\nu-1} \exp\left[i\frac{x}{2}\left(t+\frac{1}{t}\right)\right] dt,$$

it becomes $rhs = \left(\frac{k}{2\pi r}\right)^{\frac{1}{2}} (-i)(-i)^{-\frac{1}{2}} \left(\frac{-i}{\pi}\right)^{-1} e^{-\frac{i\pi}{4}} H_{-\frac{1}{2}}^{(1)}(kr) = \pi \left(\frac{k}{2\pi r}\right)^{\frac{1}{2}} H_{-\frac{1}{2}}^{(1)}(kr).$
Since $H_{-\frac{1}{2}}^{(1)}(x) = \left(\frac{2}{\pi x}\right)^{\frac{1}{2}} e^{ix}, \quad rhs = \pi \left(\frac{k}{2\pi r}\right)^{\frac{1}{2}} \left(\frac{2}{\pi kr}\right)^{\frac{1}{2}} e^{ikr} = \frac{e^{ikr}}{r} = lhs.$

A-2:
$$2i\frac{e^{ikr}}{k} = \frac{2}{\sqrt{\pi}}\int_{(0)}^{\infty} \exp\left(-r^2t^2 + \frac{k^2}{4t^2}\right)\frac{1}{t^2}dt$$
, where *r* is real and *k* is either real or

imaginary.

;

Take
$$t^{2} = x$$
 and $dt = \frac{dx}{2\sqrt{x}}$, then
Ths $= \frac{2}{\sqrt{\pi}} \frac{1}{2} \int_{(0)}^{\infty} x^{-\frac{1}{2}} x^{-1} \exp\left(-r^{2}x + \frac{k^{2}}{4x}\right) dx = \frac{1}{\sqrt{\pi}} \int_{(0)}^{\infty} x^{-\frac{3}{2}} \exp\left[\frac{kr}{2}\left(-\frac{2r}{k}x + \frac{k}{2rx}\right)\right] dx.$
As $x = \frac{ky}{2r}$, if (I) $k = ilkl$:
Ths $= \frac{1}{\sqrt{\pi}} \left(\frac{k}{2r}\right)^{1-\frac{3}{2}} \int_{(0)}^{-i\infty} y^{-\frac{3}{2}} \exp\left[\frac{kr}{2}\left(-y + \frac{1}{y}\right)\right] dy = \left(\frac{i2r}{\pi k}\right)^{\frac{1}{2}} \int_{(0)}^{\infty} z^{-\frac{3}{2}} \exp\left[\frac{ikr}{2}\left(z + \frac{1}{z}\right)\right] dz,$
with $y = -iz$. Or (II) $k = lkl$:
Ths $= \frac{1}{\sqrt{\pi}} \left(\frac{k}{2r}\right)^{1-\frac{3}{2}} \int_{(0)}^{\infty} y^{-\frac{3}{2}} \exp\left[\frac{kr}{2}\left(-y + \frac{1}{y}\right)\right] dy = \left(\frac{i2r}{\pi k}\right)^{\frac{1}{2}} \int_{(0)}^{\infty} z^{-\frac{3}{2}} \exp\left[\frac{ikr}{2}\left(z + \frac{1}{z}\right)\right] dz$
 $= \left(\frac{i2r}{\pi k}\right)^{\frac{1}{2}} \int_{(0)}^{\infty} z^{-\frac{3}{2}} \exp\left[\frac{ikr}{2}\left(z + \frac{1}{z}\right)\right] dz,$ the last equation is due to
 $0 = \oint = \int_{(0)}^{i\infty} + \int_{im}^{m+im} + \int_{m}^{(0)}$, and the two integrals in the middle are zero
because of $z^{-\frac{3}{2}}$. In both cases, the integrals can be substituted by the Hankel function in
A-1, rhs $= \left(\frac{i2r}{\pi k}\right)^{\frac{1}{2}} H_{\frac{1}{2}}^{(1)} (kr) \left(-\frac{i}{\pi}\right)^{-1} e^{\frac{i\pi}{4}} = -\left(\frac{2\pi r}{k}\right)^{\frac{1}{2}} H_{\frac{1}{2}}^{(1)}$. Since $H_{\frac{1}{2}}^{(1)}(x) = \frac{1}{i} \left(\frac{2}{\pi x}\right)^{\frac{1}{2}} e^{ix}$,
This $= -\left(\frac{2\pi r}{k}\right)^{\frac{1}{2}} \frac{1}{i} \left(\frac{2}{\pi kr}\right)^{\frac{1}{2}} e^{ikr} = 2i \frac{e^{ikr}}{k} = lhs$. If it is case (I), the equation is equal to
 $2\frac{e^{ikr}}{k!}$.

A-3:
$$\frac{2}{\sqrt{\pi}} \int_{E}^{\infty} \exp\left(-r^{2}t^{2} + \frac{k^{2}}{4t^{2}}\right) dt = \frac{1}{2r} \left[e^{ikr} \operatorname{erfc}\left(rE + \frac{ik}{2E}\right) + c.c.\right], \text{ where } r \text{ and } E \text{ are}$$

positive real numbers and k is either real or imaginary.

According to the definition of the complimentary error function, we start with

$$e^{ikr}\operatorname{erfc}\left[rE + \frac{ik}{2E}\right] = \frac{2}{\sqrt{\pi}}e^{ikr}\int_{rE + \frac{ik}{2E}}^{\infty}e^{-x^{2}}dx. \text{ With } x = rt + \frac{ik}{2t}, \text{ this equation becomes}$$

$$\frac{2}{\sqrt{\pi}}e^{ikr}\int_{rE + \frac{ik}{2E}}^{\infty}\exp\left(-r^{2}t^{2} + \frac{k^{2}}{4t^{2}} - ikr\right)d\left(rt + \frac{ik}{2t}\right) = \frac{2}{\sqrt{\pi}}\int_{E}^{\infty}\exp\left(-r^{2}t^{2} + \frac{k^{2}}{4t^{2}}\right)\left(r - \frac{ik}{2t^{2}}\right)dt$$
(A-3.1)

Also from the integral definition, $e^{-ikr} \operatorname{erfc}\left[rE - \frac{ik}{2E}\right] = \frac{2}{\sqrt{\pi}} e^{-ikr} \int_{rE-\frac{ik}{2E}}^{\infty} e^{-x^2} dx$. Taking

$$x = rt - \frac{ik}{2t}, \text{ we then have } e^{-ikr} \operatorname{erfc}\left[rE - \frac{ik}{2E}\right] = \frac{2}{\sqrt{\pi}} \int_{E}^{\infty} \exp\left(-r^{2}t^{2} + \frac{k^{2}}{4t^{2}}\right) \left(r + \frac{ik}{2t^{2}}\right) dt$$
(A-3.2)

By summing (A-3.1) and (A-3.2), we reach the original equation.

A-4:
$$\frac{2}{\sqrt{\pi}}\int_{(0)}^{E}\exp\left(-r^{2}t^{2}+\frac{k^{2}}{4t^{2}}\right)\frac{\mathrm{d}t}{t^{2}}=\frac{-1}{ik}\left[e^{ikr}\operatorname{erfc}\left(-rE-\frac{ik}{2E}\right)+e^{-ikr}\operatorname{erfc}\left(rE-\frac{ik}{2E}\right)\right].$$

Use the result of A-2, then rhs =
$$2i\frac{e^{ikr}}{k} - \frac{2}{\sqrt{\pi}}\int_{E}^{\infty} \exp\left(-r^{2}t^{2} + \frac{k^{2}}{4t^{2}}\right)\frac{dt}{t^{2}}$$
. The last

integral can be replaced by the substraction of (A-3.1) from (A-3.2), the equation becomes

rhs =
$$-2\frac{e^{ikr}}{ik} - \frac{1}{ik}\left[-e^{ikr}\operatorname{erfc}\left(rE + \frac{ik}{2E}\right) + e^{-ikr}\operatorname{erfc}\left(rE - \frac{ik}{2E}\right)\right]$$
. With the identity

2 - $\operatorname{erfc}(x) = 2\operatorname{erfc}(0)$ - $\operatorname{erfc}(x) = \operatorname{erfc}(-x)$, we have

rhs =
$$-\frac{1}{ik} \left\{ e^{ikr} \left[2 - \operatorname{erfc} \left(rE + \frac{ik}{2E} \right) \right] + e^{-ikr} \operatorname{erfc} \left(rE - \frac{ik}{2E} \right) \right\}$$

$$= -\frac{1}{ik} \left[e^{ikr} \operatorname{erfc} \left(-rE - \frac{ik}{2E} \right) + e^{-ikr} \operatorname{erfc} \left(rE - \frac{ik}{2E} \right) \right] = \operatorname{lhs}.$$

A-5:
$$\iint \exp\left(-i\mathbf{k}^{\parallel}\cdot\mathbf{r}^{\parallel}-r^{\parallel^{2}}t^{2}\right)d\mathbf{r}^{\parallel}=\frac{\pi}{t^{2}}\exp\left(\frac{-k^{\parallel^{2}}}{4t^{2}}\right), \text{ where } \mathbf{k}^{\parallel}=\mathbf{x}k^{x}+\mathbf{y}k^{y}$$

and $\mathbf{r}^{\parallel} = \mathbf{x}\mathbf{x} + \mathbf{y}\mathbf{y}$.

The two-dimensional integral is the product of two one-dimensional integrals since the integration variables are separable.

 $\begin{aligned} \ln s &= \int_{-\infty}^{\infty} \exp\left(-ik^{x}x - x^{2}t^{2}\right) dx \int_{-\infty}^{\infty} \exp\left(-ik^{y}y - y^{2}t^{2}\right) dy. \end{aligned}$ Consider a complex contour integration (z = a + ib, both a and b are real, but a is a variable while b is a constant): $0 &= \oint \exp\left(-z^{2}\right) dz \\ &= \int_{-\infty}^{\infty} \exp\left(-z^{2}\right) dz + \int_{-\infty}^{\infty+ib} \exp\left(-z^{2}\right) dz + \int_{-\infty+ib}^{-\infty+ib} \exp\left(-z^{2}\right) dz \\ &= \int_{-\infty}^{\infty} \exp\left(-a^{2}\right) da + \int_{-\infty+ib}^{-\infty+ib} \exp\left[-(a + ib)^{2}\right] d(a + ib) \\ &= \int_{-\infty}^{\infty} \exp\left(-a^{2}\right) da + \int_{-\infty}^{\infty} \exp\left[-(a + ib)^{2}\right] da. \end{aligned}$ Continuing our derivation, $\int_{-\infty}^{\infty} \exp\left(-ik^{x}x - x^{2}t^{2}\right) dx &= \int_{-\infty}^{\infty} \exp\left[-\left(xt + \frac{ik^{x}}{2t}\right)^{2}\right] d(xt) \frac{1}{t} \exp\left(\frac{-k^{x^{2}}}{4t^{2}}\right) \\ &= \int_{-\infty}^{\infty} \exp\left(-x^{2}t^{2}\right) d(xt) \frac{1}{t} \exp\left(\frac{-k^{x^{2}}}{4t^{2}}\right). \end{aligned}$ The last equation is the result of the contour

integration which we just proved. With the fact that

$$\int_{-\infty}^{\infty} \exp(-u^2) du = 2 \int_{0}^{\infty} \exp(-u^2) du = 2 \frac{\sqrt{\pi}}{2}, \text{ we conclude that}$$
$$\text{lhs} = \frac{\sqrt{\pi}}{t} \exp\left(\frac{-k^{x^2}}{4t^2}\right) \frac{\sqrt{\pi}}{t} \exp\left(\frac{-k^{y^2}}{4t^2}\right) = \text{rhs.}$$

A-6: Numerical evaluation of the complementary error function with a complex argument.

By definition,
$$\operatorname{erfc}(a+ib) = \frac{2}{\sqrt{\pi}} \int_{a+ib}^{\infty} \exp(-t^2) dt$$
, where both *a* and *b* are real

numers. From a triangular closed contour on the complex plane, the integral can be

expressed as
$$\operatorname{erfc}(a+ib) = \frac{2}{\sqrt{\pi}} \left\{ \int_{a+ib}^{a} \exp(-t^2) dt + \int_{a}^{\infty} \exp(-t^2) dt \right\}$$
. The last integral

is just erfc(a), and the other one becomes

$$\int_{a+ib}^{a} \exp(-t^{2}) dt = \int_{ib}^{0} \exp[-(x+a)^{2}] dx = i \int_{b}^{0} \exp[-(iy+a)^{2}] dy = i \int_{b}^{0} \exp(y^{2} - a^{2} - 2iay) dy$$
$$= \exp(-a^{2}) \int_{b}^{0} \exp(y^{2}) [i\cos(2ay) + \sin(2ay)] dy. \quad \text{Finally},$$
$$\operatorname{erfc}(a+ib) = \operatorname{erfc}(a) - \frac{2}{\sqrt{\pi}} \exp(-a^{2}) \Big\{ i \int_{0}^{b} \exp(y^{2}) [\cos(2ay)] dy$$
$$+ \int_{0}^{b} \exp(y^{2}) (\sin(2ay)) dy \Big\}.$$

The last two integrals are evaluated by the Romberg integration method while erfc(a) is obtained from a numerical fitting based on the Chebyshev approximation.²⁰

t

Appendix B. Programs for Surface Local Field, the Linearly Reflected Field and Surface Second Harmonic Field Calculations

B-1. COMMON.H--Universal include file:

#include <stdio.h>
#include <math.h>
#include <complex.h>
#include <stdlib.h>
#include <alloc.h>

#define pi 3.141592653589793 #define im complex(0.0, 1.0) #define eps 1.0e-10 #define Nmax 10 #define artif 1.0e-15 #define Nnm 2

// square root of -1.
// fraction of tolerance.
// maximum order in summation routine.
// to zero the artificial numbers.
// only two dipole wave modes to be solved.

void nrerror(char[]); double dot_pr(double *, double *, int, int); double *vector_dbl(int, int); complex far *vector_cmplx(int, int); int *vector_int(int, int); complex far **matrix_cmplx(int, int, int, int); double far **matrix_dbl(int, int, int, int); void cmplx_ffree(complex far **, int, int, int); void dbl_ffree(double far **, int, int, int); void dbl_ffree(double far **, int, int, int); void mat_cmplx_save(complex far **, int, int, int, int); void mat_cmplx_read(complex far **, int, int, int, int); void vector_3_save(complex far *, double *, int, int); void sp_real_save(complex far **, double *, int, int); void p_real_save(complex far **, double *, int, int);

void ludcmp(complex far **, int, int *, double *);²⁰ void lubksb(complex far **, int, int *, complex far *);²⁰ void matrix_inv_cmplx(complex far **, int);²⁰ void lineq(complex far **, complex far *, int, int);²⁰

B-2. BASIM.CPP--Routines to read the input data file.

#include "common.h"	
#include <conio.h></conio.h>	
double lc_a;	// lattice constant along $s_1=x$ -axis.
double alpha, beta;	// planar lattice structure, $S=lc a*(n+m*alpha,m*beta,0)$. Eq.(2.18).
double wave_vect;	// wave number normalized by lc a.
double k_wave[3];	// [0]x, [1]y, [2]z.
double diff_r[3];	// position vector at n=m=0.
double E_cut;	// Ewald summation coefficient(by 1/lc_a).

double zswitch; // Ewald one-fold or three-fold transformation, normalized by lattice constant lc_a . double theta, phi, rfr_n1, rfr_n2, euler[3]; int mpq, mr, L; // 2+8*(0+1+...+mpq) is the number of normal modes in the bulk. complex m_beta[3][3][3];

void basis(void)

{

int i, j, h; double b, s_angle, lamda, elec_volt, mbr, mbi; char fin[20], fout[20], none[80]; FILE *in, *out; printf("input file name: "); scanf("%s", fin); if ((in = fopen(fin, "rt")) == NULL)nrerror("Cannot open input file."); fscanf(in,"%s %lf",none,&lc a); // in Angstroms. fscanf(in,"%s %lf",none,&b); // lattice constant along s_2 axis. fscanf(in,"%s %lf",none,&s_angle); // angle between s 1 and // s 2 in degrees. alpha=b*cos(s_angle*pi/180.0)/lc_a; beta=b*sin(s_angle*pi/180.0)/lc_a; fscanf(in,"%s %lf",none.&elec_volt); // incident photon energy. lamda=1.240e4/elec volt: // wave-length in Angstroms. wave_vect=(2.0*pi/lamda)*lc_a; // normalized by lc a. fscanf(in,"%s %lf",none,&phi); // angle between plane of incidence and s 1=x-axis. fscanf(in,"%s %lf",none,&theta); // angle of incidence in degrees. fscanf(in,"%s %lf",none,&E cut); fscanf(in,"%s %lf",none,&zswitch); fscanf(in, "%s %d", none, & mpg); fscanf(in,"%s %d",none,&L); //number of layers in free surface region. fscanf(in,"%s %lf".none,&rfr n1); fscanf(in,"%s %lf",none,&rfr_n2); fscanf(in,"%s", none); for (h=0; h<=2; h++) for (i=0; i<=2; i++) for (j=0; j<=2; j++) { fscanf(in,"%lf %lf", &mbr, &mbi); m_beta[h][i][j] = complex(mbr, mbi); fscanf(in,"%s", none); for $(j=0; j \le 2; j++)$ fscanf(in, "%lf", &euler[j]); fclose(in); printf("lc_a\tb\talpha\tbeta\telec_volt,phi\ttheta\tL E_cut zswitch"); printf("\n%7.4f,%7.4f,%7.4f,%7.4f,%7.4f,%7.4f,%7.4f,%3d,%7.4f,%7.4f\n", lc_a,b,alpha,beta,elec_volt,phi,theta,L,E_cut,zswitch); printf("mpq=%d\trfr_n1=%g\trfr_n2=%g",mpq,rfr_n1,rfr_n2); printf("\tEuler angles=(%g %g %g)", euler[0], euler[1], euler[2]); phi *= pi/180.0;// convert into radiance. theta *= pi/180.0; $k_wave[0] = wave_vect*sin(theta)*cos(phi);$ k_wave[1] = wave_vect*sin(theta)*sin(phi);

```
k_wave[2] = -wave_vect*cos(theta); // field coming in from z>0.
mr = 2*mpq*(mpq+1); // number of reciprocal lattice
```

// number of reciprocal lattice points
// included in the summation besides (0.0).

```
return;
```

}

{

void rotate(complex mb[3][3][3])

// transformation matrix from a molecular coordinate system to a laboratory coordinate system.

double et[3][3], cp, ct, cf, sp, st, sf, na; int h, i, j, hh, ii, jj; complex ob[3][3][3];

```
na = pow(lc_a*1.0e-8, -2.0);
                                                // number density in cm^2.
for (h=0; h<=2; h++) for (i=0; i<=2; i++)
          for (j=0; j \le 2; j++) ob[h][i][j] = mb[h][i][j]*na;
for (j=0; j<=2; j++) euler[j] *= pi/180.0;
cp = cos(euler[0]);
                                               // phi.
sp = sin(euler[0]);
ct = cos(euler[1]);
                                               // theta.
st = sin(euler[1]);
cf = cos(euler[2]);
                                               // psi.
sf = sin(euler[2]);
et[0][0] = cp*cf-sp*ct*sf;
et[0][1] = -cp*sf-sp*ct*cf;
et[0][2] = sp*st;
et[1][0] = sp*cf+cp*ct*sf;
et[1][1] = -sp*sf+cp*ct*cf;
et[1][2] = -cp*st;
et[2][0] = st*sf;
et[2][1] = st^{*}cf;
et[2][2] = ct;
for (h=0; h<=2; h++) for (i=0; i<=2; i++)
         for (j=0; j<=2; j++) {
                  mb[h][i][j] = 0.0;
                  for (hh=0; hh<=2; hh++)
                            for (ii=0; ii<=2; ii++)
                                     for (jj=0; jj<=2; jj++)
mb[h][i][j] += et[h][hh]*et[i][ii]*et[j][jj]*ob[hh][ii][jj];
         }
return;
```

B-3. PUTF.IN--A input file.

}

lc_a,_in_Angstroms: 2.5 lattice_constant_along_s_2_axis_in_Angstroms,_b: 2.5 angle_between_s_1_and_s_2_in_degree,_s_angle: 90.0 incident_photon_energy_in_electron-volts,_elec_volt: 2.0 angle_between_plane_of_incidence_and_s_1=x-axis,_phi: 0.0 angle_of_incidence_in_degree,_theta: 45.0 E_cut,_Ewald_summation_coefficient: 2.0 zswitch: 1.0
mpq=maximum(lpl+lql)_in_bulk_calculation: 4
L=number_of_layers_in_free_surface_region: 10
rfr_n1=bulk_refractive_index_at_fundamental_frequence: 2.5
rfr_n2=bulk_refractive_index_at_harmonic_frequence: 3.0

m_beta[][][],in_esu:	0.0 0.0 0.0 0.0 0.0 0.0
	$0.0\ 0.0\ 0.0\ 0.0\ 0.0\ 0.0$
	$0.0\ 0.0\ 0.0\ 0.0\ 0.0\ 0.0$
	0.0 0.0 0.0 0.0 0.0 0.0 0.0
	$0.0\ 0.0\ 0.0\ 0.0\ 0.0\ 0.0$
	$0.0\ 0.0\ 0.0\ 0.0\ 0.0\ 0.0$
	0.0 0.0 0.0 0.0 0.0 0.0 0.0
	$0.0\ 0.0\ 0.0\ 0.0\ 0.0\ 0.0$
	0.0 0.0 0.0 0.0 50.0e-30 0.0
Euler_angles(phi,theta,psi	i),in_degree: 0.0 0.0 0.0

B-4. RFLC-B.CPP--A microscopic calculation of the linear reflection.

```
#include "common.h"
#include <conio.h>
#include <dos.h>
complex qm[Nnm], um[Nnm][3];
                                            // bulk dipole wave solutions.
complex far ***dpq, ***bpq, *kapa;
void main()
ł
         int i, j, u, v, dc;
         double sr, pr;
         void basis(void);
        basis();
        dc=mr;
        kapa = vector_cmplx(0,dc);
        dpq =(complex far***)farcalloc((unsigned long)(dc+1),sizeof(complex far**));
        bpq =(complex far***)farcalloc((unsigned long)(dc+1),sizeof(complex far**));
        for(i=0; i<=dc; i++) {
                 dpq[i] = matrix_cmplx(0,2,0,2);
                 bpq[i] = matrix\_cmplx(0,2,0,2);
         }
        char fout[20], none[80];
        FILE *out:
        struct date d;
        getdate(&d);
str:
        printf("\n file name to save: ");
        scanf("%s", fout);
        if ((out = fopen(fout, "wt")) == NULL) {
                 printf("\n...Cannot open output file, try again.");
                 goto str;
        }
```

```
printf("title of the file, no whitespace and no comma, please:");
          scanf("%s", none);
          fprintf(out,"GRAPH 4\nASCII\n%s\n%d-%d-%d\n 5\n", none, d.da_mon, d.da day,
                                                                                            d.da_year);
          fprintf(out,"angle of incidence,p-mic,s-mic,p-mac,s-mac");
          fprintf(out,"\n 91, 91, 91, 91, 91");
          for (i=0; i<=90; i++) {
                   if ((i\%5)==0) printf(" %d", i);
                   fprintf(out,"\n%d", i);
                  theta = double(i)*pi/180.0;
                  mr=dc:
                  k_wave[0] = wave_vect*sin(theta)*cos(phi);
                  k_wave[1] = wave_vect*sin(theta)*sin(phi);
                  k_wave[2] = -wave_vect*cos(theta);
                  lnrflc(&pr, &sr);
                  fprintf(out,",%22.15lg,%22.15lg", pr, sr);
                  frsnl(&pr, &sr);
                  fprintf(out,",%22.15lg,%22.15lg", fabs(pr), fabs(sr));
         fprintf(out,"\n 0");
         fclose(out);
         farfree(kapa);
                                             // free the dynamic memory.
         for(i=dc; i \ge 0; i - ) 
                  cmplx_ffree(dpq[i],0,2,0);
                  cmplx_ffree(bpq[i],0,2,0);
         }
         farfree(dpg);
         farfree(bpg);
         return:
void lnrflc(double *prfl, double *srfl)
         double **rj, er;
                                             // **rj are the position vectors of characteristic dipoles.
         int i, j, u, v, ii, dc, rc, flg=0;
         complex far **dpf:
         complex fld[3], dum[Nnm][3], kw, kl, dd[Nnm];
         void dipole(double**, complex far**, int);
        dpf = matrix_cmplx(0,1,1,3*(L+1)+Nnm);
        r_j=matrix_dbl(0,L,0,2);
                                             //position vector of lattice points at n=m=0.
         for (i=0; i<=L; i++) {
                                             // Eq.(2.17) and Fig. 2.2.
                 r_i[i][0]=0.0;
                                            // s_1 or x-axis.
                 rj[i][1]=0.0;
                                            // y-axis.
                 rj[i][2] = -1.0*i;
                                            // z-axis.
         }
        dipole(rj, dpf, flg);
                                            // calculate the characteristic dipole vector at rj.
        for (i=0; i<=nm; i++) {
                 dd[i] = complex(1.0)-exp(-im*(qm[i]-kapa[0]));
                 for (v=0; v <=2; v++) {
                          dum[i][v] = complex(0.0);
                          for (j=0; j \le 2; j++) dum[i][v] += dpq[0][v][j]*um[i][j];
                  ł
```

}

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```
if (L>=0) kl = -complex(k_wave[0]*rj[L][0]+k_wave[1]*rj[L][1])
                                              -kapa[0]*complex(rj[L][2]-1.0);
         else kl = complex(0.0.0.0):
for (ii=0; ii<=1; ii++) {
                                              // p-polarization (ii=0) and s-polarization (ii=1) incidence.
         for (u=0; u \le 2; u++) {
                   fld[u] = complex(0.0);
                   for (j=0; j<=L; j++) {
                            kw = -complex(k_wave[0]*rj[j][0]+k_wave[1]*rj[j][1])
                                              -kapa[0]*complex(ri[i][2]);
                            for (v=0; v<=2; v++)
                                                       // the reflected field is
                                     fld[u] += dpq[0][u][v]*dpf[ii][3*j+v+1]*exp(im*kw);
                                                       // the dipole field from surface layers,
                   for (i=0; i<=nm; i++) fld[u] += dpf[ii][3*(L+1)+1+i]*dum[i][u]*exp(im*kl)/dd[i];
                                                       // plus the dipole field from the bulk.
         }
         for (u=0, er=0.0; u \le 2; u++) er += norm(fld[u]);
         if (ii==0) *prfl = sqrt(er);
         if (ii==1) *srfl = sqrt(er);
ł
         cmplx ffree(dpf,0,1,1);
         dbl_ffree(rj,0,L,0);
         return;
}
void frsnl(double *erp, double *ers)
         // Fresnel's results of reflection and transmission.
{
         double ni=1.0, nt=rfr_n1, theta_i, theta_t, ets, etp;
         double eis=1.0, eip=1.0, ci, ct, loc_f;
         theta i = theta:
         theta_t = asin(sin(theta_i)*ni/nt);
         ci = cos(theta_i);
         ct = cos(theta t);
         etp = eip*2.0*ni*ci/(nt*ci+ni*ct);
         ets = eis*2.0*ni*ci/(ni*ci+nt*ct);
         *erp = eip*(nt*ci-ni*ct)/(nt*ci+ni*ct);
         *ers = eis*(ni*ci-nt*ct)/(ni*ci+nt*ct);
         return;
}
B-5. SHGRF-B.CPP--A microscopic calculation of reflected SSHG.
void main()
```

{

```
int i, j, u, v, dc;
void basis(void), rotate(complex [3][3][3]);
double rp[2], rs[2], ci, si, rps[2];
complex nlp[2][3], dd;
basis();
rotate(m_beta);  // surface susceptibility per cm^2.
dc=mr;
```

```
kapa = vector cmplx(0.dc):
         dpq =(complex far***)farcalloc((unsigned long)(dc+1).sizeof(complex far**));
         bpq =(complex far***)farcalloc((unsigned long)(dc+1).sizeof(complex far**));
         for(i=0; i<=dc; i++) {
                  dpq[i] = matrix_cmplx(0,2,0,2);
                  bpq[i] = matrix\_cmplx(0,2,0,2);
         ł
        char fout[20], none[80];
        FILE *out1, *out2;
        struct date d:
        getdate(&d):
str1:
        printf("\n file name to save: ");
        scanf("%s", fout);
        if ((out1 = fopen(fout, "wt")) == NULL) {
                 printf("\n...Cannot open output file, try again.");
                 goto str1;
        }
        printf("title of the file, no whitespace and no comma, please:");
        scanf("%s", none);
        fprintf(out1,"GRAPH 4\nASCII\n%s\n%d-%d-%d\n 7\n",
                                                     none, d.da_mon, d.da_day, d.da_year);
        fprintf(out1,"angle of incidence,pp-mic,ps-mic,pp-semi,ps-semi,pp-mac,ps-mac");
        fprintf(out1,"\n 91, 91, 91, 91, 91, 91, 91, 91");
        ci = cos(phi);
        si = sin(phi);
        for (i=0; i<=90; i++) {
        if ((i%5)==0) printf(" %d", i);
        fprintf(out1,"\n%d", i);
                 theta = double(i)*pi/180.0;
                                                              // angle of incidence
                 mr=dc;
                 k_wave[0] = wave_vect*sin(theta)*ci;
                                                              // wave vector
                 k_wave[1] = wave_vect*sin(theta)*si;
                 k_wave[2] = -wave_vect*cos(theta);
                 shgrflc(nlp, rp, rs);
                 fprintf(out1,",%g,%g", rp[0], rs[0]);
                 boundary(rps, nlp[0]);
                 fprintf(out1,",%g,%g", rps[0], rps[1]);
                blmbgn(nlp);
                                                    // macroscopic nonlinear polarization.
                boundary(rps, nlp[0]);
                fprintf(out1,",%g,%g", rps[0], rps[1]);
                wave_vect \neq 2.0;
                                                    // reset the frequency.
        fprintf(out1,"\n 0");
        fclose(out1);
        farfree(kapa);
                                                    // free the dynamic memory.
        for(i=dc; i \ge 0; i--)
                cmplx_ffree(dpg[i],0,2,0);
                cmplx_ffree(bpq[i],0,2,0);
       farfree(dpg);
       farfree(bpq);
       return;
```

}

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123

void shgrflc(complex nlp[2][3], double rp[2], double rs[2])

ł

}

}

ł

```
double **ri, rfl[3], ci, si;
                                               // **rj are the position vectors of characteristic dipoles.
          int i, j, u, v, ii, dc, rc, flg=0;
          complex far **dpf;
          complex fld[3], dd, dum, kw, kl;
          void dipole(double**, complex far**, int), basis(void);
          void shg_dpl(double**, complex[2][3], complex far **);
          dpf = matrix_cmplx(0,1,1,3*(L+1)+Nnm);
          r_j = matrix_dbl(0, L, 0, 2);
                                              //position vector of lattice points at n=m=0.
          for (i=0; i <=L; i++) {
                                              // Eq.(2.17) and Fig. 2.2.
                   r_{i}[i][0]=0.0;
                                              // s 1 or x-axis.
                   rj[i][1]=0.0;
                                              // y-axis.
                   rj[i][2] = -1.0*i;
                                              // z-axis.
          }
          dipole(rj, dpf, flg);
          shg_dpl(rj, nlp, dpf);
                                              // calculate the characteristic dipole vector of 2\omega at rj.
          if (L>=0) kl = -complex(k_wave[0]*rj[L][0]+k_wave[1]*rj[L][1])
                                                                 -kapa[0]*complex(ri[L][2]-1.0);
          else kl = complex(0.0,0.0);
          ci = cos(phi);
          si = sin(phi);
for (ii=0; ii<=1; ii++) {
                                              // p-polarization (ii=0) and s-polarization (ii=1) incidence.
         for (u=0; u<=2; u++) {
                  fld[u] = complex(0.0);
                                              // Eq.(3.26) : the reflected SSHG.
                   for (v=0; v \le 2; v++) fld[u] += dpq[0][u][v]*nlp[ii][v];
                                              // the dipole field of nonlinear (the topmost layer) response.
                  for (j=0; j<=L; j++) {
                            kw = -complex(k_wave[0]*rj[j][0]+k_wave[1]*rj[j][1])
                                                                -kapa[0]*complex(rj[j][2]);
                            for (v=0; v <=2; v++)
                                     fld[u] = dpq[0][u][v]*dpf[ii][3*j+v+1]*exp(im*kw);
                                              // and the linear response from surface layers,
                  for (i=0; i <= nm; i++)
                           dd = complex(1.0) - exp(-im*(qm[i]-kapa[0]));
                           dum = complex(0.0);
                           for (v=0; v \le 2; v++) dum += dpq[0][u][v]*um[i][v];
                           fld[u] += dpf[ii][3*(L+1)+1+i]*dum*exp(im*kl)/dd;
                  }
                                             // plus the dipole field from the bulk.
         rp[ii] = abs(-(fld[0]*ci+fld[1]*si)*cos(theta)+fld[2]*sin(theta));
         rs[ii] = abs(fld[1]*ci-fld[0]*si);
         cmplx ffree(dpf,0,1,1);
         dbl_ffree(rj,0,L,0);
         return:
void boundary(double rps[2], complex nlp[3])
        // Eqs.(3.10 and 3.11).
```

}

{

```
void blmbgn(complex nlp[2][3])
```

// Nonlinear polarization generated by the bulk local field in the continuous medium model.

```
double etp, ets, et[3], tm, cm, sm, ni=1.0, nt=rfr_n1, nt2=rfr_n2;
int h, i, j;
tm = asin(sin(theta)*ni/nt);
frsnl(&etp, &ets);
et[0] = etp*cos(tm)*cos(phi);
et[1] = etp*cos(tm)*sin(phi);
et[2] = etp*sin(tm);
                                             // p-polarization input.
for (h=0; h<=2; h++)
         for (i=0,nlp[0][h]=complex(0.0); i <=2; i++)
                  for (j=0; j<=2; j++)
                           nlp[0][h] += m_beta[h][i][j]*et[i]*et[j];
for (h=0; h<=2; h++)
                                             // Lorentz local field factor.
         nlp[0][h] *= (nt2*nt2+2.0)*(nt*nt+2.0)*(nt*nt+2.0)/27.0;
et[0] = -ets*sin(phi);
et[1] = ets*cos(phi);
et[2] = 0.0;
                                             // s-polarization input.
for (h=0; h<=2; h++)
         for (i=0.nlp[1][h]=complex(0.0); i <=2; i++)
                  for (j=0; j \le 2; j++) nlp[1][h] += m_beta[h][i][j]*et[i]*et[j];
for (h=0; h<=2; h++)
                                             // Lorentz local field factor.
         nlp[1][h] *= (nt2*nt2+2.0)*(nt*nt+2.0)*(nt*nt+2.0)/27.0;
return;
```

}

B-6. SHG-DIPO.CCP--To calculate the electric dipole moments at 2ω.

```
void shg_dpl(double **r, complex nlp[2][3], complex far **dpf)
// nlp is the nonlinear polarization.
// **r is position vectors of lattice points at n=m=0.
{
    double pl_alpha, *rz, G;
    int i, j, u, v, ii, h;
    int rc, dc;
    complex recipr(int, int, int*), direct(int, int, int*);
    complex far **f, **m_alpha, **af;
    complex far **f, complex far**,complex far**,complex far**);
    void make_af(double *,complex far**,complex far**,complex far**);
    void make_f(complex far **, double **);
```

```
void bulk(complex far **, complex [3][3], double);
 m_alpha = matrix_cmplx(1,3,1,3); // molecular polarizability tensor.
 rz = vector dbl(0,L);
 for (i=0; i<=L; i++) rz[i] = r[i][2]; // along the z-axis.
 pl_alpha = (rfr_n1*rfr_n1-1.0)*3.0/((rfr_n1*rfr_n1+2.0)*4.0*pi);
                                    // Lorentz-Lorenz formula, 1/lc_a^3 is number density.
 for (u=1; u \le 3; u++)
                                    // an diagonal matrix.
          for (v=1; v \le 3; v++)
                  if (u==v) m_alpha[u][v] = complex(pl_alpha);
                  else m alpha[u][v] = complex(0.0);
matrix_inv_cmplx(m_alpha, 3); // invert the tensor.
for (ii=0; ii<=1; ii++) {
         for (u=1; u \le 3; u++) { // local field at the first layer.
                  e_{loc[u-1]=complex(0.0)};
                  for (v=1; v \le 3; v++) e_{loc[u-1]} = m_{alpha[u][v]}*dpf[ii][v];
          }
         for (h=0; h<=2; h++) { // nonlinear dipole of the topmost layer.
                  nlp[ii][h] = complex(0.0);
                  for (i=0; i<=2; i++)
                           for (j=0; j<=2; j++)
                                    nlp[ii][h] += m_beta[h][i][j]*e_loc[i]*e_loc[j];
         }
}
wave_vect *= 2.0;
for (h=0; h<=2; h++) k_wave[h] *= 2.0;
for (ii=0; ii<=2; ii++) diff r[ii]=0.0;
for (u=0; u\le 2; u++) for (v=0; v\le 2; v++) c[u][v] = direct(u,v,&dc)+recipr(u,v,&rc);
pl_alpha = (rfr_n2*rfr_n2-1.0)*3.0/((rfr_n2*rfr_n2+2.0)*4.0*pi);
                                    // Lorentz-Lorenz formula, 1/lc_a^3 is number density.
for (u=1; u<=3; u++)
                                    // a diagonal matrix.
         for (v=1; v <=3; v++)
                  if (u==v) m_alpha[u][v] = complex(pl_alpha);
                  else m_alpha[u][v] = complex(0.0);
matrix_inv_cmplx(m_alpha, 3); // invert the tensor.<sup>20</sup>
mr = 2*mpq*(mpq+1);
bulk(m_alpha, c, rfr_n2);
f = matrix\_cmplx(1,3*(L+1),1,3*(L+1)); // transformation tensor between surface layers at 2\omega
if (L \ge 0) make f(f, r);
af = matrix_cmplx(1,3*(L+1)+nm+1,1,3*(L+1)+nm+1);
make af(rz, af, f, m alpha);
                                  // left-hand side of Eqs.(3.25).
dc = 3*(L+1)+1;
for (ii=0; ii<=1; ii++) {
        for (i=0; i<=L; i++)
                                   // applied field by nonlinear dipole layer;
                 for (u=1; u \le 3; u++) {
                                          // right-hand side of Eqs.(3.25).
                          dpf[ii][3*i+u] = complex(0.0);
                          for (v=1; v \le 3; v++) dpf[ii][3*i+u] += f[3*i+u][v]*nlp[ii][v-1];
                  }
        for (i=0; i<=nm; i++) {
                 dpf[ii][dc+i] = complex(0.0);
```

```
if (i<=1) for (u=0; u<=2; u++) for (v=0; v<=2; v++)

dpf[ii][dc+i] += um[i][u]*bpq[0][u][v]*nlp[ii][v];
```

```
lineq(af, dpf[ii], dc+nm, 1):
```

): // iterative improvement²⁰ once! // dpf has dipole moments of the surface layers at 2ω .

}

```
free(rz);
cmplx_ffree(m_alpha,1,3,1);
cmplx_ffree(f,1,3*(L+1),1);
cmplx_ffree(af,1,dc+nm,1);
return;
```

B-7. DMPLE2.CPP--To calculate the linear dipole moments in the surface region.

{

//

ł

```
double pl_alpha, e_xt[3], *rz, G;
int i, j, u, v, ii;
complex far **f, **af, **m alpha;
int rc. dc:
complex recipr(int, int, int*), direct(int, int, int*);
void make_af(double *,complex far**,complex far**,complex far**);
void make_f(complex far **, double **):
void bulk(complex far **, complex [3][3], double);
complex c[3][3];
rz = vector dbl(0,L);
for (i=0; i<=L; i++) rz[i] = r[i][2]; // along z-axis.
m_alpha = matrix_cmplx(1,3,1,3); // molecular polarizability tensor.
for (ii=0; ii<=2; ii++) diff_r[ii]=0.0;
for (u=0; u\le 2; u++) for (v=0; v\le 2; v++) c[u][v] = direct(u,v,&dc)+recipr(u,v,&rc);
pl_alpha = (rfr_n1*rfr_n1-1)*3.0/((rfr_n1*rfr_n1+2)*4.0*pi);
                                    // Lorentz-Lorenz formula, 1/lc_a^3 is number density.
for (u=1; u \le 3; u++) {
                                    // a diagonal matrix.
         for (v=1; v <=3; v++) {
                  if (u==v) m_alpha[u][v] = complex(pl_alpha);
                  else m_alpha[u][v] = complex(0.0);
         }
matrix_inv_cmplx(m_alpha, 3); // invert the tensor.<sup>20</sup>
if (flg==0) bulk(m_alpha, c, rfr_n1);
                           // nm+1 is the number of normal mode solutions in the bulk.
f = matrix_cmplx(1,3*(L+1),1,3*(L+1));
                                    // transformation tensor between surface layers.
if (L>=0) make_f(f, r);
af = matrix_cmplx(1,3*(L+1)+nm+1,1,3*(L+1)+nm+1);
make_af(rz, af, f, m_alpha);
                                   // left-hand side of Eqs.(2.67).
dc=3*(L+1)+1:
ii=0;
                                   // p_polarization only.
for (ii=0; ii<=1; ii++) {
        if (ii=0) {
```

```
e_xt[0] = \cos(\text{theta}) \cos(\text{phi});
                            e_xt[1] = cos(theta)*sin(phi);
                            e_xt[2] = sin(theta);
                                              // external field with p_polarization.
                   if (ii==1) {
                            e_xt[0] = -sin(phi);
                            e_xt[1] = cos(phi);
                            e xt[2] = 0.0;
                                              // external field with s_polarization.
                   for (i=0; i<=L; i++)
                                              // get the external field. right-hand side of Eqs.(2.67).
                            for (u=0; u \le 2; u++) dpf[ii][3*i+u+1] =
                                     complex(e_xt[u])*exp(im*complex(dot_pr(k_wave,r[i],0,2)));
                  for (i=0; i<=nm; i++) {
                            dpf[ii][dc+i] = complex(0,0);
                           if (i \le 1) for (u = 0; u \le 2; u + 1) dpf[ii][dc+i] + um[i][u]*complex(e_xt[u]);
                  lineq(af, dpf[ii], 3*(L+1)+nm+1, 1);
                                                                // iterative improvement<sup>20</sup> once!
                                                                 // af is intact.
         }
         free(rz);
         cmplx_ffree(m_alpha,1,3,1);
         cmplx_ffree(af, 1, 3*(L+1)+nm+1, 1);
         cmplx_ffree(f, 1, 3*(L+1), 1);
         return:
}
void make_f(complex far **f, double **r)
         // Eqs.(2.34), (2.35-37), and (2.38-2.39).
{
         int i, j, ii, u, v;
         int rc, dc;
         complex recipr(int, int, int*), direct(int, int, int*);
         for (ii=0; ii<=2; ii++) diff_r[ii]=0.0;
        for (u=0; u<=2; u++) for (v=0; v<=2; v++) f[u+1][v+1] = direct(u,v,&dc)+recipr(u,v,&rc);
        for (j=0; j<=L; j++) for (u=1; u<=3; u++) for (v=1; v<=3; v++) f[3*j+u][3*j+v] = f[u][v];
        for (u=0; u<=2; u++)
                  for (j=1; j <=L; j++) {
                           for (ii=0; ii<=2; ii++) diff_r[ii]=r[0][ii]-r[j][ii];
                           for (v=0; v<=2; v++) f[u+1][3*j+v+1] = direct(u,v,&dc)+recipr(u,v,&rc);
        for (i=1; i<=L; i++) {
                 for (ii=0; ii<=2; ii++) diff_r[ii]=r[i][ii]-r[0][ii];
                 for (u=0; u<=2; u++) for (v=0; v<=2; v++)
                                             f[3*i+u+1][v+1] = direct(u,v,\&dc)+recipr(u,v,\&rc);
        for (i=1; i < =L; i++)
                 for (u=0; u<=2; u++)
                          for (j=i+1; j<=L; j++)
                                    for (v=0; v<=2; v++) f[3*i+u+1][3*j+v+1] = f[u+1][3*(j-i)+v+1];
        for (i=2; i<=L; i++)
                 for (u=0; u<=2; u++)
                          for (j=1; j<=i-1; j++)
                                    for (v=0; v<=2; v++) f[3*i+u+1][3*j+v+1] = f[3*(i-j)+u+1][v+1];
```

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return;

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}

}

```
void make_af(double *rz, complex far**af, complex far**f, complex far**m_alpha)
        // left-hand side of Eqs.(2.67) or Eqs.(3.25).
        complex dum, umb, ubu, dd, bb;
         double rm;
        int rc, dc, i, j, ii, u, v, ndx[20];
        for (i=0; i<=L; i++)
                 for (u=1; u \le 3; u++)
                          for (j=0; j<=L; j++) {
                                   for (v=1; v<=3; v++) {
                                           if (i=j) af[3*i+u][3*j+v] = m_alpha[u][v]-f[u][v];
                                           else af[3*i+u][3*j+v] = -f[3*i+u][3*j+v];
                                   }
                                           // surface layer-surface layer interaction.
                          }
        dc=3*(L+1)+1:
        rm=rz[L]-1.0;
                                           //-(L+1)
        for (i=0; i<=L; i++)
                 for (u=0; u \le 2; u++)
                         for (ii=0; ii<=nm; ii++) {
                                  af[3*i+u+1][dc+ii] = complex(0.0);
                                  for (j=0; j<=mr; j++) {
                                           dd = complex(1.0)-exp(-im*(qm[ii]-kapa[j]));
                                           dum = complex(0.0);
                                           for (v=0; v<=2; v++) dum += dpq[j][u][v]*um[ii][v];
                                           af[3*i+u+1][dc+ii] =
                                                    dum*exp(im*kapa[j]*complex(rz[i]-rm))/dd;
                                  }
                                           // only p=q=0 is included!
                         ł
                                           // bulk region to surface interaction.
       ndx[0]=ndx[1]=0;
                                           // only the propagating waves included.
       for (i=0; i<=nm; i++) {
                ii=ndx[i];
                for (j=0; j<=L; j++)
                         for (v=0; v<=2; v++) {
                                  umb = complex(0.0);
                                  for (u=0; u<=2; u++) umb += um[i][u]*bpq[ii][u][v];
                                 af[dc+i][3*j+v+1] = -umb*exp(im*kapa[ii]*complex(rz[j]));
                         }
                                          // surface layers to bulk interaction.
       for (i=0; i<=nm; i++) {
               ii=ndx[i];
               for (j=0; j<=nm; j++) {
                        bb = complex(1.0) - exp(-im*(qm[j]+kapa[ii]));
                        ubu = complex(0.0);
                        for (u=0; u<=2; u++)
                                 for (v=0; v \le 2; v++) ubu += um[i][u]*bpq[ii][u][v]*um[j][v];
                        af[dc+i][dc+j] = -ubu*exp(im*kapa[ii]*complex(rm))/bb;
               }
       }
                                          // bulk-bulk interaction.
      return;
```

B-8. ROOT.CPP--To calculate the bulk dipole moments from the decomposed dipole waves solutions.

```
#define sgn(x) (x >=0.0) ? 1.0 : -1.0
complex ***td, ***tb, *tk, ialpha_c[3][3];
```

{

```
double xq, xold, qf, sg, ipi;
int i, j, u, v, ii, *kndx, p, q, dc=mr;
complex f[2], df[2];
kndx = new int[dc+1];
tk = new complex[dc+1];
td = (complex ***) new complex ** [dc+1];
tb = (complex ***) new complex ** [dc+1];
for (i = 0; i \le dc; i++)
         td[i] = (complex **) new complex *[3];
         tb[i] = (complex **) new complex *[3];
         for (ii = 0; ii < 3; ii++) {
                  td[i][ii] = new complex[3];
                  tb[i][ii] = new complex[3];
         }
for (u=0; u<=2; u++) for (v=0; v<=2; v++) ialpha_c[u][v]=m_alpha[u+1][v+1]-c[u][v];
i=0;
for (i=0; i<=mpq; i++) {
         for (p=i; p>=-i; p--) {
                  q=i-abs(p);
                  bkfdb(p,q,j);
                  for (ii=0; ii<j; ii++)
                           if (tk[j]==tk[ii]) {
                                    for (u=0; u<=2; u++)
                                              for (v=0; v \le 2; v++) {
                                                      td[ii][u][v] += td[i][u][v];
                                                      tb[ii][u][v] += tb[i][u][v];
                                              }
                                    j--;
                           }
                 j++;
        for (p=i-1; p>=(1-i); p--) {
                  q=abs(p)-i;
                  bkfdb(p,q,j);
                  for (ii=0; ii<j; ii++)
                           if (tk[j]==tk[ii]) {
                                    for (u=0; u<=2; u++)
                                             for (v=0; v<=2; v++) {
                                                      td[ii][u][v] += td[j][u][v];
                                                      tb[ii][u][v] += tb[j][u][v];
                                             }
```

j--;

```
}
                              i++;
                    }
          }
          mr=j-1;
          for (i=0; i<=mr; i++) {
                   kndx[i]=0;
                   sg=abs(tk[i]);
                   for (j=0; j \le mr; j++) if (abs(tk[j]) \le g) kndx[i]++;
          for (i=0; i<=mr; i++) {
           ii=kndx[i];
                   kapa[ii] = tk[i];
                   for (u=0; u \le 2; u++)
                            for (v=0; v<=2; v++) {
                                     dpq[ii][u][v] = td[i][u][v];
                                     bpq[ii][u][v] = tb[i][u][v];
                             }
          }
          qf = rfr_n*wave_vect*sqrt(1.0-pow(sin(theta)/rfr_n, 2.0));
                                              // z_component of bulk macroscopic wave-vector.
          dtrmn(complex(-qf), &f[0], &df[0]);
                                                        // find roots with negative
          xold=xq=-qf;
                                              // real parts and negative imaginary parts.
         f[1]=f[0];
         df[1]=df[0];
fun1:
         xq = xold-real(f[1]/df[1]);
                                              // find bracket for root #1.
         dtrmn(complex(xq), &f[1], &df[1]);
         if ((real(f[1]) * real(f[0]) > 0.0) \&\& (abs(f[1]/df[1]) > artif)) {
                   xold = xq;
                   f[0] = f[1];
                   df[0] = df[1];
                   goto fun1;
         }
         qm[0]=rtsafe(dtrmn, complex(xold), complex(xq), qf*eps);
                                                                          // root polishing.<sup>20</sup>
         if (theta==0.0) {
                                                                          // for degenerate qms'.
                  um[0][0] = complex(-sin(phi), 0.0);
                  um[0][1] = complex(cos(phi), 0.0);
                  um[0][2] = complex(0.0,0.0);
         }
         else pl_vect(qm[0], um[0]);
         sg = sgn(real(df[0]));
         xq=real(qm[0]);
fun2:
         xq = sg*fabs(real(qm[0])+qf);
                                              // until sign changed in slop.
         dtrmn(complex(xq), \&f[1], \&df[1]);
         if ((real(df[1])*real(df[0])) >= 0.0) goto fun2;
         f[0]=f[1];
         xold=xa:
fun3:
         xq = xold-real(f[1]/df[1]);
                                              // find bracket for root #2.
         dtrmn(complex(xq), \&f[1], \&df[1]);
         if ((real(f[1])*real(f[0]) > 0.0) \&\& (abs(f[1]/df[1]) > artif)) 
                  xold = xq;
                  f[0] = f[1];
                  df[0] = df[1];
```
```
goto fun3;
          }
          qm[1]=rtsafe(dtrmn, complex(xold), complex(xq), qf*eps);
                                                                          // root polishing.<sup>20</sup>
          if (theta==0.0) {
                                                                          // for degenerate qms'.
                   um[1][0] = complex(cos(phi), 0.0);
                   um[1][1] = complex(sin(phi), 0.0);
                   um[1][2] = complex(0.0.0.0);
          }
          else pl_vect(qm[1], um[1]);
         nm=1;
         delete [] kndx;
stp:
         delete [] tk;
                                              // FREE MEMORY
         for (i = 0; i \le dc; i++) {
                  for (ii = 0; ii < 3; ii++) {
                            delete [] td[i][ii];
                            delete [] tb[i][ii];
                   }
                  delete [] td[i];
                  delete [] tb[i];
         }
         delete [] td;
         delete [] tb;
         return;
}
complex doit(complex far **a)
                                              // determinant of a 3x3 matrix.
{
         complex dm;
         dm = a[1][1]*a[2][2]*a[3][3]+a[1][2]*a[2][3]*a[3][1]
                  +a[1][3]*a[3][2]*a[2][1]-a[1][1]*a[3][2]*a[2][3]
                  -a[1][2]*a[2][1]*a[3][3]-a[1][3]*a[2][2]*a[3][1];
         return dm;
}
void dtrmn(complex qwz, complex *dtr, complex *df)
                                             // Matrix and its determinant of Eq.(2.58).
{
        complex far **a;
        complex ds[3], dd, bb;
        int i, j, u, v, h, ii;
        a = matrix_cmplx(1,3,1,3);
        for (i=1; i<=3; i++) {
                   u = i-1;
                  for (j=1; j<=3; j++) {
                           v = j - 1;
                           a[i][j]=ialpha_c[u][v];
                           for (ii=0; ii<=mr; ii++) {
                                    dd = exp(im*(qwz-tk[ii]))-1.0;
                                    bb = exp(-im*(qwz+tk[ii]))-1.0;
                                    a[i][j]-=(td[ii][u][v]/dd+tb[ii][u][v]/bb);
                           }
                   }
        }
```

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```
*dtr = doit(a);
```

{

```
for (h=0; h<=2; h++) {
                   for (i=1; i<=3; i++) {
                            u = i - 1:
                            for (j=1; j<=3; j++) {
                                      v = j - 1;
                                     if (u != h) a[i][j]=ialpha_c[u][v];
                                     else a[i][j]=complex(0.0,0.0);
                                     for (ii=0; ii<=mr; ii++) {
                                               dd = exp(im*(qwz-tk[ii]))-1.0;
                                               bb = exp(-im*(qwz+tk[ii]))-1.0;
                                               if (u != h) a[i][j] = (td[ii][u][v]/dd + tb[ii][u][v]/bb);
                                               else a[i][j] + td[ii][u][v] * im * (dd + 1.0)/(dd * dd)
                                                                 -tb[ii][u][v]*im*(bb+1.0)/(bb*bb);
                                     }
                            }
                   }
                  ds[h] = doit(a);
         df = ds[0] + ds[1] + ds[2];
                                              // the first derivative.
         cmplx_ffree(a,1,3,1);
         return:
void pl_vect(complex qwz, complex udw[3])
         // Obtain the polarization vectors of the decomposed dipole waves according to Eq.(2.55).
         complex far **a;
        complex dd, bb, sum;
         double d, dum, big;
         int i, j, u, v, *indx, ii;
        a = matrix_cmplx(1,3,1,3);
        indx = vector_int(1,3);
        for (i=1; i<=3; i++) {
                   u = i - 1;
                  for (j=1; j<=3; j++) {
                           v = i - 1;
                           a[i][j]=ialpha_c[u][v];
                           for (ii=0; ii<=mr; ii++) {
                                    dd = exp(im*(qwz-tk[ii]))-1.0;
                                    bb = exp(-im*(qwz+tk[ii]))-1.0;
                                    a[i][j] = (td[ii][u][v]/dd+tb[ii][u][v]/bb);
                           }
                  }
```

// Find the biggest element in column.

for (i=0; i<=2; i++) udw[i] = complex(0.0,0.0);

for $(j=1; j \le 3; j++)$ if ((dum=abs(a[j][i])) > big) big=dum;

u=0;

for (i=1; i<=3; i++) {

big=0.0;

if (big == 0.0) { u++;

```
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```

```
for (ii=0; ii<=2; ii++) if (ii==(i-1)) udw[ii] = complex(1.0,0.0);
                   }
         if (u>0) goto hmm:
         ludcmp(a, 3, indx, \&d);^{20}
                                             // This returns d as 0 for singular matrix.
         dum = norm(a[1][1]);
         for (j=2; j<=3; j++) if ((d=norm(a[j][j])) < dum) dum = d;
         for (i=3; i>=1; i--) {
                                             // Back-substitution.20
                  sum = complex(0.0, 0.0);
                  for (j=i+1; j<=3; j++) sum -= a[i][j]*udw[j-1];
                  if (fabs(norm(a[i][i])-dum) < dum*artif) udw[i-1] = complex(1.0,0.0);
                  else udw[i-1] = sum/a[i][i];
         }
hmm:
         dum = 0.0;
         for (i=0; i<=2; i++) dum += norm(udw[i]);
         d = sqrt(dum);
         for (i=0; i<=2; i++) udw[i] \neq complex(d);
         for (i=0; i<=2; i++) {
                  if (fabs(real(udw[i]))<eps) udw[i]=complex(0.0,imag(udw[i]));
                  if (fabs(imag(udw[i]))<eps) udw[i]=complex(real(udw[i]),0.0);
         free(indx+1);
        cmplx_ffree(a,1,3,1);
        return;
}
void bkfdb(int p, int q, int j)
                 // D and B tensors of Eq.(2.45).
{
        complex kpg[3], dr;
        double kkd;
        int ii, u, v;
        kpq[0]=complex(k_wave[0]+2.0*pi*p);
        kpq[1]=complex(k_wave[1]+2.0*pi*(q-alpha*p)/beta);
        for (ii=0, dr=complex(0.0,0.0); ii<=1; ii++) dr += kpq[ii]*kpq[ii];
        kkd=wave_vect*wave_vect-real(dr);
        if (kkd \ge 0.0) tk[j] = complex(sqrt(kkd));
        else tk[j] = im*sqrt(fabs(kkd));
        kpq[2]=tk[j];
                                            // for the upper triangular matrix.
        for (u=0; u \le 2; u++)
                 for (v=0; v<=2; v++) {
                          td[j][u][v] = -kpq[u]*kpq[v];
                          if (u==v) td[j][u][v]+=complex(wave_vect*wave_vect);
                          td[j][u][v] *= im*complex(2.0*pi/beta)/tk[i];
        kpq[2]=-tk[j];
                                            // for the lower triangular matrix.
        for (u=0; u \le 2; u++)
                 for (v=0; v<=2; v++) {
                          tb[j][u][v] = -kpq[u]*kpq[v];
                          if (u==v) tb[j][u][v]+=complex(wave_vect*wave_vect);
                          tb[j][u][v] *= im*complex(2.0*pi/beta)/tk[i];
                 }
```

```
return;
```

B-9. Subroutines for the lattice sums in direct and reciprocal space.

```
complex direct(int u, int v, int *h)
         // Sum over the direct lattice space with Eq.(2.34).
         // The 2-D lattice vector is (n+alpha*m, beta*m, 0)*lc_a.
ł
         double k=wave_vect, E=E_cut;
         complex f(0.0, 0.0), df, ff(0.0, 0.0);
         complex nmsum(int, int, int, int), erfc_com(complex);
         int n, m, N=0;
         *h = 0:
         if (fabs(diff_r[2]) > zswitch) return f;
         if ((diff_r[2]==0.0 \&\& diff_r[1]==0.0) \&\& diff_r[0]==0.0) {
                  N=1:
                 if (u==v) ff = complex(4.0*E*(E*E-k*k)/(3.0*sqrt(pi))*exp(k*k/(4.0*E*E)))
                          -complex(2.0/3.0)*im*k*k*(erfc_com(-im*complex(k/(2.0*E)))-1.0);
         }
                 // Eq.(2.39).
                 // The substraction of (2/3)ik^3 is to include the radiation damping
                 // in the electric dipole radiation treatment.
         else N=0;
         do {
                 df = complex(0.0, 0.0);
                 for (m=N, n=N; n>=(-N); n--) df += nmsum(u, v, n, m);
                 for (m=(N-1), n=(-N); m >=(-N); m --) df += nmsum(u, v, n, m);
                 for (m=(-N), n=(-N+1); n \le N; n++) df += nmsum(u, v, n, m);
                 for (m=(-N+1), n=N; m<=(N-1); m++) df += nmsum(u, v, n, m);
                 f += df:
                 N++:
                 if (N > Nmax)
                 nrerror (" DIRECT converges slowly. Reset zswitch or E_cut.");
         \| while (N \le 2 \| ((fabs(real(df)) > fabs(real(f)*eps)) \| (fabs(imag(df)) > fabs(imag(f)*eps))));
        *h = N-1;
        if (fabs(real(f)) < artif) f = complex(0.0, imag(f));
        if (fabs(imag(f)) < artif) f = complex(real(f), 0.0);
        return f+ff;
                                           // This matrix element is normalized by lc_a^3.
}
complex nmsum(int u, int v, int n, int m)
        // Eq.(2.34).
{
        complex erfc com(complex);
        double *S, *M, T, T2, T3;
        complex f1, f2, f;
        double k=wave_vect, E=E_cut, k2, E2;
        int i:
        S = new double[3];
        M = new double[3];
        S[0]=n+alpha*m;
        S[1]=beta*m;
```

```
S[2]=0.0;
          for (i=0; i<=2; i++) M[i]=diff_r[i]-S[i];
         T=sqrt(dot_pr(M, M, 0, 2));
         k2=k*k:
         E2=E*E;
         T2=T*T;
         T3=T2*T:
         f1=M[u]*M[v]*(complex(3.0/T2-k2)-im*complex(3.0*k/T));
         if (u==v) f1 += (k2*T2-1.0+im*k*T);
         f2=M[u]*M[v]*(complex(3.0/T2+2.0*E2)-im*complex(k/T));
         if (u==v) f2 -= 1.0;
         f1 *= exp(im*k*T)*erfc_com(T*E+im*complex(k/(2.0*E)))*complex(1/T3);
         f2 = complex(exp(-T2*E2+k2/(4.0*E2))*2.0*E/(sqrt(pi)*T2));
         f = \exp(im*dot_pr(k_wave, S, 0, 2))*real(f1+f2);
         delete[] S;
         delete∏ M:
         return f;
complex recipr(int u, int v, int *h)
         // Perform two dimensional summation over reciprocal lattice space.
         // The reciprocal lattice vector is (beta*p, q-alpha*p, 0)*2*pi/(lc_a*beta), .
         complex f(0.0, 0.0), df;
         complex pqsum(int, int, int, int);
         int p, q, N=0;
         do {
                  df = complex(0.0, 0.0);
                  for (q=N, p=N; p>=(-N); p--) df += pqsum(u, v, p, q);
                  for (q=(N-1), p=(-N); q = (-N); q = 0) df += pqsum(u, v, p, q);
                  for (q=(-N), p=(-N+1); p \le N; p++) df += pqsum(u, v, p, q);
                  for (q=(-N+1), p=N; q <=(N-1); q++) df += pqsum(u, v, p, q);
                  f += df:
                  N++;
                  if (N > Nmax)
                  nrerror (" RECIPR converges slowly. Reset zswitch or E_cut.");
         | while (N \le 1 \parallel ((fabs(real(df)) > fabs(real(f)*eps)) \parallel (fabs(imag(df)) > fabs(imag(f)*eps))));
         *h = N-1:
         if (fabs(real(f)) < artif) f = complex(0.0, imag(f));
         if (fabs(imag(f)) < artif) f = complex(real(f), 0.0);
        return f*im*complex(pi/beta);
                                           // This matrix element is normalized by lc_a^3.
complex pqsum(int u, int v, int p, int q)
        // Eqs.(2.29, 2.35, 2.36 and 2.37).
        complex erfc_com(complex);
        complex f1(0.0, 0.0), kapa, delta1, delta2;
        complex kpg[3], dr;
```

{

}

{

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```
double kkd, k=wave_vect, E=E_cut, zz=fabs(diff_r[2]);
         int g, ii;
         if (zz > zswitch) g=2;
                                            // use Eq.(2.29).
         else g=1;
                                            // use Eqs.(2.35, 2.36 and 2.37).
         kpq[0]=complex(k_wave[0]+2.0*pi*p);
         kpq[1]=complex(k_wave[1]+2.0*pi*(q-alpha*p)/beta);
         for (ii=0, dr=complex(0.0,0.0); ii<=1; ii++) dr += kpq[ii]*kpq[ii];
         kkd=k*k-real(dr);
         if (kkd >= 0.0) kapa=complex(sqrt(kkd));
         else kapa=im*sqrt(fabs(kkd));
         if (diff_r[2] < 0.0) kpq[2] = -kapa;
         else kpq[2]=kapa;
         f1 \rightarrow kpq[u] kpq[v];
         if (u==v) f1 += complex(k*k);
         if (g==2) {
                 f1 *= complex(2.0)/kapa;
                 goto out:
         }
        delta1 = erfc_com(-im*kapa/complex(2.0*E)-zz*E)*exp(im*kapa*zz);
        delta2 = erfc\_com(-im*kapa/complex(2.0*E)+zz*E)*exp(-im*kapa*zz);
        if ((u==2) \land (v==2)) f1 *= (delta1-delta2)/kapa; // exclusive or
        else f1 *= (delta1+delta2)/kapa;
        if ((u==2) & (v==2)) f1 += exp(-zz*zz*E*E+kapa*kapa/complex(4.0*E*E))
                                                             *im*complex(4.0*E/sqrt(pi));
        for (ii=0, dr=complex(0.0,0.0); ii<=g; ii++) dr += kpq[ii]*diff_r[ii];
out:
        f1 *= exp(im*dr);
        return f1;
```

```
}
```

{

B-10. Evaluate the complementary error function with a complex argument.

```
static double az;
double snep(double t) { return exp(t*t)*sin(2.0*az*t);}
double csep(double t) { return exp(t*t)*cos(2.0*az*t);}
```

```
complex erfc_com(complex z)
        // Appendix A-6.
        double snep(double), csep(double);
        double erfcc(double);
        double qromb (double (*)(double), double, double); // A Romberg integration routine.<sup>20</sup>
        complex cx;
        double bz=imag(z), aden;
        az=real(z);
        if (az == 0.0) {
                 aden=0.0;
                 cx=complex(1.0, 0.0);
```

```
}
else {
```

```
cx = complex(erfcc(az));
aden=qromb(snep, 0.0, bz);
```

```
}
cx -= complex(aden, qromb(csep, 0.0, bz))*complex(exp(-az*az)*2.0/sqrt(pi));
return cx;
```

ł

}

```
double erfcc(double x)
```

// Returns the complementary error function erfc(x), based on Chebyshev fitting,²⁰ // with fractional error everywhere less than 1.2e-7.

```
double t, z, ans;
z=fabs(x);
t=1.0/(1.0+0.5*z);
ans=t*exp(-z*z-1.26551223+t*(1.00002368+t*(0.37409196+t*(0.09678418+t*(-0.18628806+t*(0.27886807+t*(-1.13520398+t*(1.48851587+t*(-0.82215223+t*0.17087277)))))))));
return x >= 0.0 ? ans : 2.0-ans;
```

Appendix C. Programs to Calculate the Temperature of *a*-C:H Films Heated by a Train of Short Laser Pulses

STATIC SUB heating ()

```
CALL ScanTranslate
         CLS: LOCATE 8, 18, 1
         PRINT "Enter <cr> to start or <esc> to exit: "
sqry:
         cq = INKEY$
         SELECT CASE cg$
                  CASE CHR$(27): GOTO dacquit
                 CASE "": GOTO sqry
                 CASE ELSE
         END SELECT
         rdgss = rdgss * .0001#
                                           'laser beam size; convert to cm.
         rlocate = rlocate * .0001#
                                           'radial location for the calc.; convert to cm.
         zdepth = zdepth * .0001#
                                           'depth into the substrate for the calc.; convert to cm.
         tlavpr = tlavpr * .001
                                           'average laser power; convert to watt.
         thickfm = thickfm * .0000001#
                                           'film thickness; convert to cm.
         ipnum = INT(plwidth) \setminus 10
                                           'how many short pulses in a train.
         plnorm = 0
         FOR i = 0 TO ipnum
                 plnorm = plnorm + pwr(i * 10! / plwidth)
         NEXT i
         plnorm = tlavpr * (1 - 10 ^ (-absorb)) * .002 / plnorm
                                                                'energy absorbed in each train.
        FOR i = 0 TO ipnum
                                                             repetition rate of 500 Hz (0.002 sec).
                 qheat(i) = plnorm * pwr(i * 10! / plwidth) 'energy absorbed in each pulse.
        NEXT i
        b(1, 0) = \text{tempint: } b(0, 0) = 0; j = 0; \text{pts}(0) = 1000; \text{pts}(1) = \text{pts}(0)
                                                                              'calculate 1001 points.
        FOR i = 0 TO ipnum
                 pltime(i) = 0
        NEXT i
hell:
        i = i + 1
        SELECT CASE mttr$
                 CASE "diamond": CALL diamond(b(1, j - 1))
                 CASE "graphite": CALL graphite(b(1, j - 1))
                 CASE "amcarbon": CALL amcarbon(b(1, j - 1))
                 CASE ELSE: GOTO dacquit
        END SELECT
        CALL silica(b(1, j - 1))
        IF b(0, j - 1) < plwidth THEN
                                                   'inside the pulse train.
                 b(0, j) = b(0, j - 1) + drtint
                jnum = INT(b(0, j)) \setminus 10
                IF b(0, j) - (INT(b(0, j)) \setminus 10) * 10 < drtint THEN jnum = jnum - 1
                FOR i = 0 TO jnum
                         pltime(i) = pltime(i) + drtint
                 NEXT i
                b(1, j) = tempint + addtemp(jnum)
                IF zdepth = 0 AND rlocate < rdgss AND b(0, j) - (INT(b(0, j)) \setminus 10) * 10 < drtint
```

```
THEN
                         CALL pulseinst(b(1, j), qheat(jnum + 1))
                         b(1, j) = tempfnl
                 END IF
        ELSE
                                                   'outside the pulse train.
                 b(0, j) = b(0, j - 1) + drtout
                 FOR i = 0 TO ipnum
                         pltime(i) = pltime(i) + drtout
                 NEXT i
                 b(1, j) = tempint + addtemp(ipnum)
        END IF
        IF j MOD 20 = 0 THEN PRINT "point counts=", j
        IF j < pts(0) THEN GOTO hell
        CALL MaxMin
dacquit:
                 CALL ScanTranslate: CALL WriteScreen
        EXIT SUB
END SUB
STATIC FUNCTION addtemp (ima)
                                                  'Eq.(4.6)
        DIM transi AS DOUBLE, dzt AS DOUBLE, dfkt AS DOUBLE, adtmp AS DOUBLE
        dtemp = 0
        FOR i = 0 TO ima
                 transi = pltime(i) * .00000001# 'time after the arriving of the pulse train;
                                                   'convert to second.
                 dzt = dffsili * transi
                 dfkt = 4 * dffsvty * transi + rdgss * rdgss
                adtmp = qheat(i) * EXP(-(zdepth ^ 2) / (4 * dzt)) * EXP(-(rlocate ^ 2) / dfkt)
                dzt = 2.2 * cpsili * SQR(dzt) + density * cpcty * thickfm
                                                                          '2.2 is density of quartz.
                adtmp = adtmp / ((pi) ^ 1.5 * dzt * dfkt)
                dtemp = dtemp + adtmp
        NEXT i
        addtemp = dtemp
        EXIT FUNCTION
END FUNCTION
STATIC SUB amcarbon (tempk)
                                                           ' a-C:H; 200 K to 4000 K.
        acoe(1) = -11.7: acoe(2) = 8.3: acoe(3) = -1.52: acoe(4) = .08 'same as the graphite
        bcoe(1) = 444: bcoe(2) = -393: bcoe(3) = 117: bcoe(4) = -11.6
                         ' average value of graphite for which // and \perp to the layer planes
        logtemp = LOG(tempk) / ln10
        ijk = 4
        CALL fpoly(logtemp, ijk)
        cpcty = 0: cndcty = 0
        FOR i = 1 TO ijk
                cpcty = cpcty + acoe(i) * afunc(i)
                                                           ' specific heat
                cndcty = cndcty + bcoe(i) * afunc(i)
                                                           ' thermal conductivity
        NEXT i
```

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dffsvty = cndcty / (density * cpcty) EXIT SUB ' thermal diffusivity

END SUB

STATIC SUB diamond (tempk) ' 200 K to 4000 K by extrapolation. acoe(1) = -3.47: acoe(2) = -3.39: acoe(3) = -.72: acoe(4) = 3.59acoe(5) = -1.38: acoe(6) = .15bcoe(1) = 387: bcoe(2) = -339: bcoe(3) = 99.5: bcoe(4) = -9.75bcoe(5) = 0; bcoe(6) = 0logtemp = LOG(tempk) / ln10ijk = 6CALL fpoly(logtemp, ijk) cpcty = 0: cndcty = 0FOR i = 1 TO ijkcpcty = cpcty + acoe(i) * afunc(i)' specific heat cndcty = cndcty + bcoe(i) * afunc(i)' thermal conductivity NEXT i dffsvty = cndcty / (density * cpcty) ' thermal diffusivity EXIT SUB

END SUB

```
STATIC SUB fpoly (xi, ima)
```

routine to calculate a polynomial of degree ima-1, with ima coefficients.

afunc(1) = 1 FOR j = 2 TO ima afunc(j) = afunc(j - 1) * xi NEXT j EXIT SUB

END SUB

STATIC FUNCTION fsgn# (gkk#, ggk#)

```
IF ggk# >= 0 THEN fsgn# = ABS(gkk#) ELSE fsgn# = -ABS(gkk#)
```

END FUNCTION

STATIC SUB graphite (tempk) '200 K to 4000 K by extrapolation.

acoe(1) = -11.7: acoe(2) = 8.3: acoe(3) = -1.52: acoe(4) = .08 bcoe(1) = 888: bcoe(2) = -787: bcoe(3) = 234: bcoe(4) = -23.3 '// to the layer planes. logtemp = LOG(tempk) / ln10 ijk = 4CALL fpoly(logtemp, ijk) cpcty = 0: cndcty = 0

```
FOR i = 1 TO ijk

cpcty = cpcty + acoe(i) * afunc(i)

cndcty = cndcty + bcoe(i) * afunc(i)

NEXT i

dffsvty = cndcty / (density * cpcty)

EXIT SUB
```

END SUB

STATIC SUB pulseinst (tempk, qht)

'to estimate the temperature at the time right after a short laser pulse

```
DIM integrl AS SINGLE, mc AS DOUBLE, spota AS DOUBLE
        spota = pi * rdgss * rdgss
       integrl = 0: tempfnl = tempk
       SELECT CASE mttr$
ntgrl:
               CASE "diamond": CALL diamond(tempfnl)
               CASE "graphite": CALL graphite(tempfnl)
               CASE "amcarbon": CALL amcarbon(tempfnl)
               CASE ELSE: EXIT SUB
       END SELECT
       CALL silica(tempfnl)
       mc = cpcty * density * thickfm
       mc = mc + cpsili * 2.2 * SQR(dffsili * .0000000001#) '2.2 is density of the quartz substrate
       mc = mc * spota
       integrl = integrl + mc
       IF qht > integrI THEN
               tempfnl = tempfnl + 1
               GOTO ntgrl
       END IF
       EXIT SUB
```

END SUB

```
STATIC FUNCTION pwr (xi)

acoe(1) = 0: acoe(2) = 10.46: acoe(3) = -35.17: acoe(4) = 36.11

acoe(5) = 5.16: acoe(6) = -29.91: acoe(7) = 13.35

ijk = 7

CALL fpoly(xi, ijk)

ppwr = 0

FOR i = 1 TO ijk

ppwr = ppwr + acoe(i) * afunc(i)

NEXT i

pwr = ppwr

EXIT FUNCTION
```

END FUNCTION

' the substrate; 200 K to 4000 K by extrapolation.

```
acoe(1) = -.54: acoe(2) = -.47: acoe(3) = -.029: acoe(4) = .54
acoe(5) = -.19: acoe(6) = .019
bcoe(1) = 99: bcoe(2) = 89: bcoe(3) = 5.4: bcoe(4) = -111
bcoe(5) = 52: bcoe(6) = -6.5
logtemp = LOG(tempk) / ln10
ijk = 6
CALL fpoly(logtemp, ijk)
cpsili = 0: cndsili = 0
FOR i = 1 TO ijk
         cpsili = cpsili + acoe(i) * afunc(i)
                                                      ' specific heat
         cndsili = cndsili + bcoe(i) * afunc(i)
                                                      ' thermal conductivity
NEXT i
cndsili = cndsili * .001
dffsili = cndsili / (2.2 * cpsili)
                                                      ' thermal diffusivity
EXIT SUB
```

END SUB

' A input data file:

*

Commands:__@ go__<cr>@

Scan Parameters :_@

beam size (radius of the Gaussian profile in micron):_50@ the total averaged incidence power (in milliwatt):_160@ away from center of the spot on the film to calc. (in micron):_50@ depth into the substrate to calc. (in micron):_0@ initial temperature (in Kelvin):_293@ time interval for calculation (in nanosec.):_@ within the pulse-train:_.5@ outside the pulse-train:_3@ pulse train duration (in nanosec.):_400@ absorbance of the film:_0.13@ thickness of the film (in Angstrom):_250@ density of the film (D:3.5, G:2.3, a-carbon:1.2-2.5):_2.3@ material of the film (diamond, graphite or amcarbon):_amcarbon@

Remark: array 0 for time, @ array 1 for temperature. @

*