# Dielectric properties of a thin film consisting of a few layers of molecules or particles

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An accurate model for the dielectric properties of a thin film consisting of a few layers of particles (or molecules) is described. The depth dependence and the anisotropic behavior of the local permittivity due to the surface environment are studied. The method is described in terms of a general multipole expansion, but the detailed derivation is carried out mainly in the framework of dipole approximation for the field interactions of particles. Both the static and harmonic cases are considered. Numerical results are presented.

## I. INTRODUCTION

The surface effect is very important for thin films with molecular structures in optical engineering and thin composite structures in microwave applications. It makes the dielectric properties for a thin film different from those for the corresponding medium of infinite extent.

For a composite medium of infinite extent, one can find the effective dielectric properties for *sparse* inclusions in the static case through some mixing formulas (see, e.g., Ref. 1) or the Lorentz formula for the electromagnetic interaction between the inclusion particles (see e.g., Refs. 2–8). If the interaction is not static or the inclusion density is not sparse, one needs to use some numerical methods to compute the effective properties of bulk media (see, e.g., Ref. 9). Much work has also been done in analyzing the effective conductivity (see, e.g., Refs. 10 and 11) and in obtaining bounds between which the effective properties for a composite medium of infinite extent must lie (see, e.g., Refs. 12 and 13).

For a thin film consisting only a few layers of particles (or molecules), the local permittivity becomes uniaxial near the two surfaces of the thin film even if the particles are isotropic. Since the local dielectric properties are different for different layers, the effective permittivity for the thin film as a whole may differ from the effective permittivity for the corresponding bulk composite medium. The depth dependence and the anisotropic behavior of the local permittivity due to the surface environment are very important in thin-film technology since they will influence, e.g., the reflection and transmission properties of the thin film. Although there is a vast literature in the surface physics studying the phenomena occurring on (or near) surfaces, not much work has been done in analyzing the surface effects on the local dielectric properties of a composite medium near the surface. The effect of the orientation of the liquid molecules on the surface has been studied in Ref. 14, where it was shown that the surface anisotropy of the liquid leads to a so-called pseudo-Brewster reflection. The surface effect on the dispersion of the polarization has been considered in Ref. 15 through an analysis of the polariton modes. In Ref. 16, the permeability for a two-dimensional granular thin film has been studied but the surface-to-bulk transition was not considered there. In Ref. 3 a slab of a few layers of dielectric ellipsoidal inclusions is considered and the dipolar approximation is used for the interaction of ellipsoids. A surface averaging (instead of a volume averaging) over each layer is used in Ref. 3 for calculating the averaged (mean) field when the total number of layers is few (however, no explicit criteria for minimal number of layers is given there for treating the multilayered composite as a bulk one). In the present paper, we will show that the local permittivity (defined through the volume averaging) is physically sound even for very few number of layers. The electromagnetic interactions of the inclusion particles are assumed to be electrostatic in all these references.

In the present paper, we describe an accurate model for the dielectric properties of a thin film consisting a few layers of particles (or molecules) for both the static and harmonic cases. We study the depth dependence (particularly in the transition zone near the surfaces) and the anisotropic behavior of the local permittivity of the thin film. We present two different models (both taking into account the low-frequency corrections to the static theory) for the computation of the local permittivity, namely, the discrete model and the continuous model. These models should be more appropriate for use in studying structures of a few layers of inclusions than the recent models (see, e.g., Refs. 4 and 5) that correct the static theory of unbounded composite media but have not included the surface variations of the effective parameters. In the present paper, we describe the method in terms of a general multipole expansion (valid even when the array of particles are dense) but give the detailed derivation mainly in the framework of the dipole approximation (when the array of particles are sparse) for the field interactions of particles.

## II. THE STATIC CASE

Consider a slab composed of a few layers of particles that are distributed periodically in the transverse $x$ and $y$ directions (see Fig. 1). These inclusion particles form a cubic lattice of finite thickness. The particles are identical and with identical orientations (if they are not of spherical shape). The particles have a smooth boundary so that the field produced by them at an arbitrary point can be expressed through the multipole expansion. It is assumed that the condition $d$

 

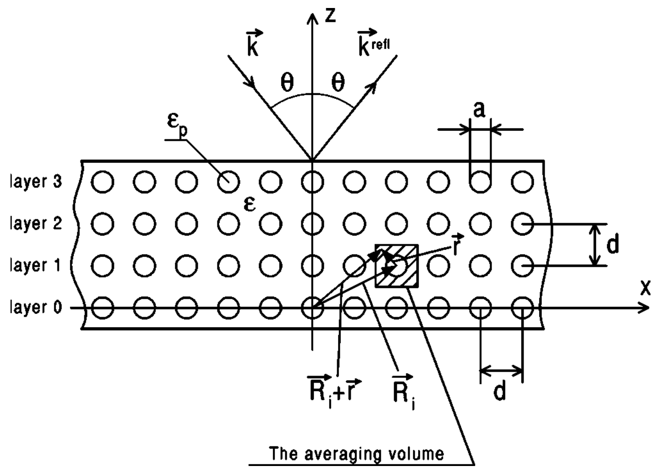


FIG. 1. Configuration for a thin film consisting of a few layers of particles in a cubic lattice.

$\geqslant 2a$ is satisfied, where $a$ is the characteristic size of the particles and $d$ is the lattice constant. This condition allows one to make a dipole approximation for the field interaction of particles, i.e., contribution of higher multipoles can be neglected at the distance $d$. This condition also allows one to avoid solving the Laplace equation for the whole inhomogeneous structure, since one can then represent the response of a particle to the local field through the particle's electric polarizability (which is assumed to be known).

### A. Field interaction

Denote the total number of the layers of particles in the thin film by $N$. The external sources (free charges) are located outside the slab. For example, the induced dipole moment for each particle is given by the following formula (see, e.g., Ref. 7),

$$\mathbf{p}=\bar{\bar{\alpha}}\cdot\mathbf{E}^{loc}, \tag{1}$$

where the polarizability $\bar{\bar{\alpha}}$ for the particles is assumed to be known and $\mathbf{E}^{loc}$ is the local field. Similarly, the higher-order multipole polarizabilities are also assumed to be known (if one wishes to take them into account). The local field for the $i$th particle (located at the position $\mathbf{R}_i$) is given by

$$\mathbf{E}_i^{loc}=\mathbf{E}^{ext}(\mathbf{R}_i)+\sum_{j\neq i}\mathbf{E}_j^{part}(\mathbf{R}_i), \tag{2}$$

where $\mathbf{E}_i^{ext}$ is the field at the center of the $i$th particle produced by the external sources and $\mathbf{E}_j^{part}$ is the field produced by the $j$th particle. The total field can be written in the following form,

$$\mathbf{E}(\mathbf{R}_i+\mathbf{r})=\mathbf{E}^{ext}(\mathbf{R}_i+\mathbf{r})+\sum_{j\neq i}\mathbf{E}_j^{part}(\mathbf{r}+\mathbf{R}_i)+\mathbf{E}_i^{part}(\mathbf{R}_i+\mathbf{r}), \tag{3}$$

where $\mathbf{r}$ is the position vector in the local cell coordinate system, which has its origin at the center of the reference cell (cf. Fig. 1). As in the classical theory for dielectric properties of a bulk medium (i.e., an infinite lattice of particles/molecules),[7] we need to introduce the averaged field and the averaged polarization. It is reasonable to use a unit lattice cell $d\times d\times d$ as the averaging volume $V_{av}$, and the averaging of the true field (the microscopic field) over the unit cell is called the averaged field (the macroscopic field).

The averaged field and polarization at an arbitrary point are defined by

$$\langle\mathbf{E}\rangle(\mathbf{R})\equiv\frac{1}{V_{av}}\int_{V_{av}}\mathbf{E}(\mathbf{R}+\mathbf{r}')d^3\mathbf{r}', \tag{4}$$

$$\langle\mathbf{P}\rangle(\mathbf{R})\equiv\frac{1}{V_{av}}\int_{V_{av}}\mathbf{P}(\mathbf{R}+\mathbf{r}')d^3\mathbf{r}', \tag{5}$$

where $V_{av}$ is the volume of the unit lattice cell centered at point $\mathbf{R}$, i.e., $V_{av}=d^3$. In some works on multiphase media (when shapes and sizes of the inclusions are different; see, e.g. Ref. 6), the averaged field is defined in terms of integration over several cells (in order to take in account the varieties of the particles). For simplicity, we consider only the case of identical inclusions in the present paper.

If the particles are not too close to each other, the contribution of the higher-order multipole moments to the averaged field is quite small compared to the contribution of the dipole moment (see, e.g., Refs. 9 and 10). Since the size of the particle is small compared with the cell size ($a\leqslant d/2$), we can assume that inside the particle the microscopic polarization $\mathbf{P}$ is uniform and equal to $\mathbf{p}/V_p$, where $V_p$ is the volume of the particle. Outside the particle we have $\mathbf{P}=\mathbf{0}$. At the center of the particle we have $\langle\mathbf{P}\rangle(\mathbf{R}_i)=\mathbf{p}/d^3$.

For the averaged field at the center of the $i$th particle one has [cf. Eq. (3)]

$$\langle\mathbf{E}\rangle(\mathbf{R}_i)=\frac{1}{V_{av}}\int_{V_{av}}\mathbf{E}^{ext}(\mathbf{R}_i+\mathbf{r})dV+\frac{1}{V_{av}}\sum_{j\neq i}\int_{V_{av}}\mathbf{E}_j^{part}(\mathbf{r}+\mathbf{R}_i)dV+\frac{1}{V_{av}}\int_{V_{av}}\mathbf{E}_i^{part}(\mathbf{R}_i+\mathbf{r})dV. \tag{6}$$

We assume that the external sources are located outside and sufficiently far from the slab. In the static or low-frequency case, the external field can be assumed to be approximately uniform inside the cell. This leads to the following approximation:

$$\langle\mathbf{E}^{ext}\rangle(\mathbf{R}_i)\approx\mathbf{E}_{ext}(\mathbf{R}_i). \tag{7}$$

Subtracting Eq. (2) from Eq. (6) and using Eq. (7), one obtains

$$\langle\mathbf{E}\rangle(\mathbf{R}_i)-\mathbf{E}_i^{loc}=\sum_{j\neq i}[\langle\mathbf{E}_j^{part}\rangle(\mathbf{R}_i)-\mathbf{E}_j(\mathbf{R}_i)]+\langle\mathbf{E}_i^{part}\rangle(\mathbf{R}_i). \tag{8}$$

Applying the Taylor expansion for $\langle\mathbf{E}_j^{part}\rangle$ around the point $\mathbf{r}=0$, one obtains

$$\langle \mathbf{E}_j^{part}\rangle|_{\mathbf{r}=\mathbf{0}} = \frac{1}{V_{av}}\int_{V_{av}}\bigg( \mathbf{E}_j^{part}|_{\mathbf{r}=\mathbf{0}} + r_\alpha \nabla_\alpha \mathbf{E}_j^{part}|_{\mathbf{r}=\mathbf{0}} + \frac{1}{2} r_\alpha r_\beta \nabla_\alpha \nabla_\beta \mathbf{E}_j^{part}|_{\mathbf{r}=\mathbf{0}} + \frac{1}{6} r_\alpha r_\beta r_\gamma \nabla_\alpha \nabla_\beta \nabla_\gamma \mathbf{E}_j^{part}|_{\mathbf{r}=\mathbf{0}} + \frac{1}{24} r_\alpha r_\beta r_\gamma r_\delta \nabla_\alpha \nabla_\beta \nabla_\gamma \nabla_\delta \mathbf{E}_j^{part}|_{\mathbf{r}=\mathbf{0}} + \cdots \bigg) dV, \tag{9}$$

where the Greek letters denote the Cartesian coordinates and the conventional contraction rule for summation over repeated indices is implied. Note that the second and fourth terms in the above equation always give zero contribution to the integral since they are odd functions of the Cartesian coordinates, and the third and fifth terms vanish if $\alpha \neq \beta$ and $\gamma \neq \delta$. Thus one obtains the following expression:

$$\langle \mathbf{E}_j^{part}\rangle|_{\mathbf{r}=\mathbf{0}} - \mathbf{E}_j^{part}|_{\mathbf{r}=\mathbf{0}} = \frac{1}{2V_{av}} \nabla_\alpha^2 \mathbf{E}_j^{part}|_{\mathbf{r}=\mathbf{0}} \int_{V_{av}} r_\alpha^2 dV + \frac{1}{24V_{av}} \nabla_\alpha^2 \nabla_\beta^2 \mathbf{E}_j^{part}{}_{\mathbf{r}=\mathbf{0}} \times \int_{V_{av}} r_\alpha^2 r_\beta^2 dV + \cdots. \tag{10}$$

In the static case, the field $\mathbf{E}_j^{part}(\mathbf{r})$ satisfies the following Laplace equation,

$$\Delta \mathbf{E}_j^{part}(\mathbf{R}) \equiv \sum_{\alpha=1}^{3} \nabla_\alpha^2 \mathbf{E}_j^{part}(\mathbf{R}) = \mathbf{0}. \tag{11}$$

In the static case the above Laplace equation holds at an arbitrary point outside the source of the field $\mathbf{E}_j^{part}$ (i.e., $j$th particle), and thus it holds inside the $i$-numbered cell ($i \neq j$). For a time-harmonic case we show below that the error in such a Laplace equation approximation is of order $(kd)^2$.

Thus, all the terms (including the first two terms) in Eq. (10) which have $2^n$ times operation $\nabla$, where $n = 1,2,3,\ldots,$ become zero. Excluding all these zero terms and keeping only the first nonzero term, one obtains the following approximation:

$$\langle \mathbf{E}\rangle_j^{part}|_{\mathbf{r}=\mathbf{0}} - \mathbf{E}_j^{part}|_{\mathbf{r}=\mathbf{0}} \approx \frac{1}{720V_{av}} \nabla_\alpha^2 \nabla_\beta^2 \nabla_\gamma^2 \mathbf{E}_j|_{\mathbf{r}=\mathbf{0}} \int_{V_{av}} r_\alpha^2 r_\beta^2 r_\gamma^2 dV. \tag{12}$$

The integral in Eq. (12) equals $d^9/13\,824$ and the right side (normalized by the field amplitude) of Eq. (12) is of the order of $10^{-7}$. The sixth-order spatial derivatives of the dipole field can be expressed in terms of the field generated by the electrostatic multipole of the same order. The sum of these terms due to all the surrounding particles [$j \neq i$; cf. expression (8)] can be expressed as a lattice sum of the sixth-order multipole field multiplied by a factor of $10^{-7}$. Thus we can assume that this sum is negligible. It then follows from Eq. (8) that

$$\langle \mathbf{E}\rangle(\mathbf{R}_i) - \mathbf{E}_i^{loc} = \langle \mathbf{E}_i^{part}\rangle \tag{13}$$

for the static case.

The sum of the differences given in Eq. (12) is negligible if the slab thickness is much larger than the lattice constant $d$. This is due to the fact that the Lorentz formula is quite accurate inside a lattice cell that is far away from the slab surface [see, e.g., Ref. 10 and Eq. (16) below]. The contribution from these terms in Eq. (12) is maximal (i.e., the Lorentz formula has maximal error) if the slab contains a single layer.

### B. Averaging the field generated by the reference particle

The term $\langle \mathbf{E}^{part}\rangle(\mathbf{R}_i)$ in Eq. (8) is the averaging (over the $i$th cell) of the field produced by the $i$th particle, i.e.,

$$\langle \mathbf{E}^{part}\rangle(\mathbf{R}_i) = \frac{1}{V_{av}}\int_{V_{av}} \mathbf{E}_i^{part}(\mathbf{R}_i + \mathbf{r}) dV.$$

The field $\mathbf{E}_i^{part}$ can be expressed in terms of the potential. Since the multipole expansion is implied in our theory, one may express the field at an arbitrary point of the cell by[8]

$$\mathbf{E}_i^{part}(\mathbf{R}_i + \mathbf{r}) = -\frac{1}{4\pi\epsilon} \boldsymbol{\nabla}\left( \frac{p_\alpha r_\alpha}{r^3} + \frac{q_{\alpha\beta} r_\alpha r_\beta}{2r^5} + \frac{o_{\alpha\beta\gamma} r_\alpha r_\beta r_\gamma}{6r^7} + \cdots \right),$$

where $p_\alpha$, $q_{\alpha\beta}$, and $o_{\alpha\beta\gamma}$ are the components of the dipole, quadrupole, and octopole moments of the reference particle, respectively, and $\epsilon$ is the permittivity for the host medium, which may differ from $\epsilon_0$ (the permittivity for vacuum) for the case when the slab is of a composite material with two components. For the case when the slab is a few layers of molecules, one has $\epsilon = \epsilon_0$ (since the host medium is a free space in this case). First we consider the dipole moment contribution. Integrating along the $\alpha$ axis for the $\alpha$ component of $\mathbf{E}_0^{part}$, one obtains

$$\langle E_{0\alpha}^{part}\rangle(\mathbf{R}_i) = -\frac{1}{4(d/2)^3}\frac{1}{4\pi\epsilon} \times \int_S \left( \frac{p_\beta r_\beta}{r_0^3} + \frac{p_\gamma r_\gamma}{r_0^3} + \frac{p_\alpha d/2}{r_0^3} \right) dr_\gamma dr_\beta,$$

where $r_0 = \sqrt{r_\gamma^2 + r_\beta^2 + (d/2)^2}$ and $S = d \times d$. After a simple integration one obtains

$$\langle E_{0\alpha}^{part}\rangle(\mathbf{R}_i) = -\frac{p_\alpha}{3\epsilon}\frac{1}{d^3}. \tag{14}$$

Since $\mathbf{p} = \mathbf{P}(\mathbf{R}_i) d^3$, it follows that

$$\langle \mathbf{E}_0^{part}\rangle(\mathbf{R}_i) = -\frac{\langle \mathbf{P}\rangle(\mathbf{R}_i)}{3\epsilon}. \tag{15}$$

Since the cell is symmetric, the contribution of the quadrupole moment to the averaged field vanishes. The octopole moment contribution to $\langle \mathbf{E}_0^{part} \rangle$ can be evaluated in a similar way, and leads to the following equation [as a correction to Eq. (15), for the same cubic cell case]:

$$\langle E_{0\alpha}^{part} \rangle = -\frac{\langle P_\alpha \rangle}{3\epsilon} - \frac{\langle O_{\alpha\alpha\alpha} \rangle}{72\epsilon d^2}.$$

If the particles are not too close to each other (for example if $d > 1.5a$, where $a$ is the characteristic size of an inclusion particle), the contribution of the octopole moment to the averaged field is quite small compared to the contribution of the dipole moment (unless the particle shape is very complex and special), and the multipole series converges rapidly. In such a case one can neglect the contributions of the octopole and other higher-order multipoles of the reference particle to the averaged field $\langle \mathbf{E}_0^{part} \rangle$ (this has been proved for the lattices of spheres and rods in Refs. 9 and 10). To simplify the analysis, we carry out the detailed derivation using the dipole approximation for the field interactions of particles in the rest of the paper with the assumption that the array of particles are sparse (for example, $d > 1.5a$). Note that the method can be easily extended to include higher-order multipoles when the array of particles are dense.

Equations (13) and (15) lead to the following Lorentz formula:

$$\mathbf{E}^{loc}(\mathbf{R}_i) - \langle \mathbf{E} \rangle(\mathbf{R}_i) = \frac{1}{3\epsilon}\mathbf{P}(\mathbf{R}_i). \tag{16}$$

In Ref. 8 the above formula is given as an expression for the difference between the local field and the averaged field for an *infinite* dielectric structure.

In Appendix A, we have estimated the error introduced by neglecting the terms in the right side of Eq. (12) for a single layer of molecules (this error is maximal for this case). Our estimation gives 8% for this error (see Appendix A). If the slab consists of $N \geqslant 4$ layers, this error turns out be negligible for all inner layers and for an entire slab (as the numerical modeling described below shows).

### C. Discrete and continuous models for the local susceptibility and permittivity

The averaged volume polarization $\langle \mathbf{P} \rangle$ is related with the averaged field through the susceptibility tensor $\bar{\bar{\kappa}}_{loc}$, which is defined by

$$\langle \mathbf{P} \rangle \equiv \bar{\bar{\kappa}}_{loc} \cdot \langle \mathbf{E} \rangle. \tag{17}$$

For the general case of anisotropic particles, one can easily obtain the following Clausius-Mossotti relation from Eqs. (1) and (16),

$$\bar{\bar{\kappa}}_{loc}(\mathbf{R}_i) = \frac{1}{d^3}\left(\bar{\bar{I}} - \frac{\bar{\bar{\alpha}}}{3d^3\epsilon}\right)^{-1} \cdot \bar{\bar{\alpha}}, \tag{18}$$

where $\bar{\bar{I}}$ is a unit dyadic. Note that the polarizability $\bar{\bar{\alpha}}$ for the particles is assumed to be known. The above expression gives the values of the local susceptibility only at some discrete points, namely, at the centers of the particles inside the thin film.

The local permittivity $\bar{\bar{\epsilon}}_{loc}$ is defined by the following well-known relations,

$$\mathbf{D} = \bar{\bar{\epsilon}}_{loc}\langle \mathbf{E} \rangle, \quad \mathbf{D} = \epsilon\langle \mathbf{E} \rangle + \langle \mathbf{P} \rangle,$$

where $\mathbf{D}$ is the electric displacement vector. It thus follows from definition (17) that

$$\bar{\bar{\epsilon}}_{loc}(\mathbf{r}) = \bar{\bar{\kappa}}_{loc}(\mathbf{r}) + \epsilon\bar{\bar{I}}. \tag{19}$$

From Eqs. (19) and (18) one determines the local permittivity at the centers of the particles inside the thin film.

We need to study the local susceptibility and permittivity at an arbitrary point. Relation (17) holds at an arbitrary point, whereas Eq. (18) holds only at the centers of the particles. Therefore, we should compute directly the averaged field and the averaged polarization at an arbitrary point [using Eqs. (4) and (5)] in order to determine the local susceptibility and permittivity at an arbitrary point. This will be addressed in Sec. III B below for the general harmonic case. Such a computation becomes simpler if the particles are dielectric spheres, since for this special case we consider the microscopic field outside the particles as a field generated by a lattice of dipoles and the microscopic field inside the particles to be uniform and related with the dipole moment by the following Rayleigh's equations,[8]

$$\mathbf{p} = 2\epsilon V_0 \frac{\epsilon_p - \epsilon}{2\epsilon_p + \epsilon}\mathbf{E}^{(p)}, \quad \mathbf{p} = -3\epsilon V_0 \frac{\epsilon_p - \epsilon}{2\epsilon + \epsilon_p}\mathbf{E}^{loc}, \tag{20}$$

where $\mathbf{E}^{(p)}$ is the total field inside the particle, $\epsilon_p$ is the permittivity of the particle, $V_0 = 4\pi b^3/3$, and $b = a/2$ is the radius of the spherical particle. Due to the symmetry and the surface effects, the permittivity tensor becomes uniaxial and depth dependent. The result of the Clausius-Mossotti relation (18) can then be used as a check.

### D. Effective permittivity for the whole slab

The depth-dependent uniaxial permittivity in a thin slab can be denoted by

$$\bar{\bar{\epsilon}} = \epsilon^t(z)\bar{\bar{I}}_t + \epsilon^n(z)\mathbf{z}_0\mathbf{z}_0,$$

where $\bar{\bar{I}}_t = \mathbf{x}_0\mathbf{x}_0 + \mathbf{y}_0\mathbf{y}_0$. One can average the above permittivity profile to find the effective permittivity of the slab as a whole (which will influence the reflection and transmission of the electromagnetic waves). The effective permittivity $\bar{\bar{\epsilon}}_{eff}$ can be obtained by the following formulas:[17]

$$\epsilon_{eff}^t = \frac{1}{D}\int_0^D \epsilon^t(z)dz, \tag{21}$$

$$\epsilon_{eff}^n = D\left(\int_0^D \frac{dz}{\epsilon^n(z)}\right)^{-1}, \tag{22}$$

where $D$ is the thickness of the thin film. There is a simple physical interpretation for the averaging formulas (21) and (22). The problem of calculating the effective permittivity along a direction normal (or parallel) to the interface for a stack of dielectric layers by averaging is analogous to the problem of calculating the total capacitance of many capacitors in series (or in parallel). It is well known that for the total capacitance the elementary capacitances are additive if they are in parallel, and for the case of capacitors in series their inverses are additive.

## III. THE HARMONIC CASE

In this section we generalize the electrostatic results (given in the previous section) to the harmonic case with time dependence $\exp(i\omega t)$.

### A. Discrete model for the permittivity

Consider a plane wave obliquely incident (from the top) on the thin film consisting of $N$ layers of particles. The layers are labeled as $m=0,1,\ldots,N-1$ from the bottom to the top, and the origin of the Cartesian coordinate system is located at the center of a particle in the layer $m=0$ (see Fig. 1). Each particle in the cubic lattice is isotropic and with a known dipole polarizability $\alpha$. In the harmonic case, we have to consider the phase-shift effects and we wish to calculate the local susceptibility and permittivity at the centers of each layers in this subsection. The incident field at the origin $x=y=z=0$ is denoted by $\mathbf{E}^0$. For simplicity we assume that the plane of incidence is the $xz$ plane. Thus, the incident field has the following form at the plane $z=0$,

$$\mathbf{E}^{inc}(x,y,0)=\mathbf{E}^0 e^{-ik_x x}, \tag{23}$$

where the transverse wave number $k_x$ is related to the incident angle. We can consider separately the $E$-polarization case when $E_y=E^0$ and the $H$-polarization case when $E_x^0=E^0k_z/k_0$, $E_z^0=E^0k_x/k_0$, where $k_z=\sqrt{k_0^2-k_x^2}$ and $k_0=\omega\sqrt{\mu_0\epsilon_0}$ is the wave number in vacuum (note that the medium outside the thin film is vacuum). Including the $z$ dependence, Eq. (23) may be rewritten in the following form for both the $E$- and $H$-polarization cases,

$$\mathbf{E}^{inc}(x,y,z)=\mathbf{E}^0 e^{-i(k_x x-k_z z)}.$$

Denote the wave number in the host medium as $k$, i.e., $k=\omega\sqrt{\epsilon\mu_0}$. The center plane for the top layer is $z=D=(N-1)d$. We consider the case when $kD\leqslant 1$, i.e., the thickness of the thin film is small compared to the wavelength.

In the harmonic case, the Laplace equation (11) for the field in the $i$th cell produced by the $j$th particle should be replaced by the following Helmholtz equation:

$$\Delta\mathbf{E}_j^{part}(\mathbf{r})=-k^2\mathbf{E}_j^{part}(\mathbf{r}). \tag{24}$$

Neglecting the terms of the order $(kd)^4$, it follows from Eqs. (10) and (24) that

$$\langle\mathbf{E}_j^{part}\rangle(\mathbf{r}=\mathbf{0})-\mathbf{E}_j^{part}(\mathbf{r}=\mathbf{0})=-\frac{(kd)^2}{6}\mathbf{E}_j^{part}(\mathbf{r}=\mathbf{0}). \tag{25}$$

Here we have used the fact that

$$\int_{V_{av}} r_\alpha^2 dV=d^5/12.$$

Thus, the Lorentz formula (16) at the point $\mathbf{R}_M$ ($x=y=0,z=Md$) must be modified and replaced by the following formula:

$$\mathbf{E}^{loc}(\mathbf{R}_M)-\langle\mathbf{E}\rangle(\mathbf{R}_M)=\frac{\mathbf{P}(\mathbf{R}_M)}{3\epsilon}-\frac{(kd)^2}{24}\sum_{j\neq M}\mathbf{E}_j(\mathbf{R}_j-\mathbf{R}_M). \tag{26}$$

At each layer, we call the particle with coordinates $x=l_1d$ and $y=0$ the $l_1$-numbered particle. Due to the periodicity in Eq. (23), at the $m$th layer we may express the dipole moment for the $l_1$-numbered particle in terms of the dipole moment for the 0-numbered particle as follows:

$$\mathbf{p}_{(m,l_1)}=\mathbf{p}_{(m,0)}e^{-il_1k_xd}. \tag{27}$$

To estimate the $z$ dependence of the susceptibility and permittivity, it is sufficient to consider relation (26) at the centers of the 0-numbered particles of each layer. We may express the field produced by each particle of the $m$th layer in terms of the corresponding dipole moment $\mathbf{p}_{(m,0)}$. Thus, we have the following relation between $\mathbf{p}_{(m,0)}$ and the field $\mathbf{E}^{(mM)}$ at the point ($x=y=0,z=Md$) produced by the $m$th layer,

$$\mathbf{E}^{(mM)}=\frac{\bar{\bar{F}}_{mM}}{\epsilon d^3}\cdot\mathbf{p}_{(m,0)}=\frac{\bar{\bar{F}}_{mM}}{\epsilon}\cdot\mathbf{P}_{(m,0)}, \tag{28}$$

where $\bar{\bar{F}}_{mM}$ is a certain dyadic to be found (we call it the *interaction dyadic*).

The dipole moment for the 0-numbered particle of the $m$th layer is related to the dipole moment for the 0-numbered particle of the 0th layer in the following form,

$$\mathbf{p}_{(m,0)}=\bar{\bar{f}}_m\cdot\mathbf{p}_{(0,0)},$$

where $\bar{\bar{f}}_m$ is called the *distribution dyadic* and is to be determined. It then follows from Eq. (26) that (replacing $\mathbf{p}_{(0,0)}$ with $\mathbf{P}_{(0,0)}d^3$)

$$\mathbf{E}^{loc}(\mathbf{R}_M)-\langle\mathbf{E}\rangle(\mathbf{R}_M)=\frac{1}{3\epsilon}\left[\bar{\bar{f}}_M+\frac{(kd)^2}{8}\times\sum_{m=0}^{N-1}\bar{\bar{F}}_{mM}\cdot\bar{\bar{f}}_m\right]\cdot\mathbf{P}_{(0,0)}. \tag{29}$$

Expressing $\mathbf{P}_{(0,0)}$ in the above equation in terms of $\mathbf{P}_{(M,0)}$, one obtains

$$\mathbf{E}^{loc}(\mathbf{R}_M)-\langle\mathbf{E}\rangle(\mathbf{R}_M)=\frac{\bar{\bar{L}}_M\cdot\mathbf{P}_{(M,0)}}{3\epsilon},$$

where the dyadic factor $\bar{\bar{L}}_M$ is given by

$$\bar{\bar{L}}_M=\left(\bar{\bar{I}}+\frac{(kd)^2}{8}\bar{\bar{f}}_M^{-1}\sum_{m=0}^{N-1}\bar{\bar{F}}_{mM}\cdot\bar{\bar{f}}_m\right). \tag{30}$$

Thus, the Clausius-Mossotti equation (18) is generalized to the following one for the harmonic case:

$$\bar{\bar{\kappa}}(z=Md)=\frac{1}{d^3}\left(\bar{\bar{I}}-\frac{\alpha}{d^3\epsilon}\bar{\bar{L}}_M\right)^{-1}\alpha. \tag{31}$$

We call $\bar{\bar{L}}_M$ the *locality factor*. Once $\bar{\bar{\kappa}}(z=Md)$ is found, one knows the local permittivity tensor $\bar{\bar{\epsilon}}(z=Md)$ from Eq. (19). If the locality factor $\bar{\bar{L}}_M$ is real for a real-valued $\alpha$ and its dependence on the incident angle is weak, the concept of the local permittivity is appropriate. A numerical scheme for computing the dyadics $\bar{\bar{F}}_{mM}$ has been described in Appendix B. Below we only present the final results (see Appendix B for the detailed derivation).

If $m \neq M$, the components for the interaction dyadic $\bar{\bar{F}}_{mM}$ can be computed by

$$F^{xx}_{mM} = \sum_{l_1=-\infty}^{+\infty} \sum_{l_2=-\infty}^{+\infty} \frac{1}{2k_z^{(l)}d} e^{-|M-m|dk_z^{(l)}} \times [(k_z^{(l)}d)^2 - (k_y^{(l)}d)^2], \tag{32}$$

$$F^{xy}_{mM} = F^{yx}_{mM} = \sum_{l_1=-\infty}^{+\infty} \sum_{l_2=-\infty}^{+\infty} \frac{1}{2k_z^{(l)}d} e^{-|M-m|dk_z^{(l)}} \times [(k_x^{(l)}d)(k_y^{(l)}d)], \tag{33}$$

where

$$k_x^{(l)} = k_x + \frac{2\pi l_1}{d}, \quad k_y^{(l)} = \frac{2\pi l_2}{d}, \quad k_z^{(l)} = \sqrt{k_x^{(l)^2} + k_y^{(l)^2} - k^2}.$$

The expression for $F^{yy}_{mM}$ (or $F^{zz}_{mM}$) is obtained by replacing $k_y^{(l)}$ (or $k_z^{(l)}$) with $k_x^{(l)}$ (or $-k_x^{(l)}$) in expression (32). The expression for $F^{xz}_{mM}$ and $F^{zx}_{mM}$ (or $F^{yz}_{mM}$ and $F^{zy}_{mM}$) is obtained by replacing $k_y^{(l)}$ (or $k_x^{(l)}$) by $ik_z^{(l)}$ in expression (33).

For the present case when the incident plane is in the $xz$ plane, one has $F^{xy}_{mM} = F^{yx}_{mM} = 0$ and $F^{yz}_{mM} = F^{zy}_{mM} = 0$. The expressions for the other components of $\bar{\bar{F}}_{mM}$ can be rewritten in the following more convenient form,

$$F^{xz}_{mM} = F^{zx}_{mM} = \sum_{l_1=-\infty}^{+\infty} \sum_{l_2=-\infty}^{+\infty} e^{-2\pi\xi^{(l)}|M-m|} \left( k_x + \frac{2\pi l_1}{d} \right), \tag{34}$$

$$F^{xx}_{mM} = \pi \sum_{l_1=-\infty}^{+\infty} \sum_{l_2=-\infty}^{+\infty} \frac{(k_x d/2\pi + l_1)^2 - (kd/2\pi)^2}{\xi^{(l)}} \times e^{-2\pi\xi^{(l)}|M-m|}, \tag{35}$$

$$F^{yy}_{mM} = \pi \sum_{l_1=-\infty}^{+\infty} \sum_{l_2=-\infty}^{+\infty} \frac{l_2^2 - (kd/2\pi)^2}{\xi^{(l)}} e^{-2\pi\xi^{(l)}|M-m|}, \tag{36}$$

$$F^{zz}_{mM} = -\pi \sum_{l_1=-\infty}^{+\infty} \sum_{l_2=-\infty}^{+\infty} \frac{(k_x d/2\pi + l_1)^2 + l_2^2}{\xi^{(l)}} \times e^{-2\pi\xi^{(l)}|M-m|}, \tag{37}$$

where

$$\xi^{(l)} = \sqrt{\left( \frac{k_x d}{2\pi} + l_1 \right)^2 + l_2^2 - \left( \frac{kd}{2\pi} \right)^2}. \tag{38}$$

It is easy to check that in the static limit $k = k_x = 0$ the above expressions reduce to Ewald's results for the interaction dyadic,[18] namely, the off-diagonal components are zeros and

$$F^{xx,yy}_{mM} = \pi \sum_{l_1=-\infty}^{+\infty} \sum_{l_2=-\infty}^{+\infty} \frac{l_1^2}{\sqrt{l_1^2 + l_2^2}} e^{-2\pi|M-m|\sqrt{l_1^2 + l_2^2}}, \tag{39}$$

$$F^{zz}_{mM} = -\pi \sum_{l_1=-\infty}^{+\infty} \sum_{l_2=-\infty}^{+\infty} \sqrt{l_1^2 + l_2^2}\, e^{-2\pi|M-m|\sqrt{l_1^2 + l_2^2}}. \tag{40}$$

If $m = M$, the components for the interaction dyadic $\bar{\bar{F}}_{mM}$ are given by (see Appendix B)

$$F^{xx}_{MM} = F^{yy}_{MM} = 0.359, \quad F^{zz}_{MM} = -0.718, \tag{41}$$

and the other components are identically zero.

After the interaction dyadic $\bar{\bar{F}}_{mM}$ is calculated, the distribution dyadic $\bar{\bar{f}}_m$ is obtained by the following formula,

$$\bar{\bar{f}}_m = \frac{\mathbf{p}_{(m,0)} \mathbf{p}_{(0,0)}}{(\mathbf{p}_{(0,0)} \cdot \mathbf{p}_{(0,0)})}, \tag{42}$$

where the distribution of the induced dipole moment $\mathbf{p}_{(m,0)}$ along the $z$ axis is determined by solving the following algebraic system:

$$\mathbf{p}_{(M,0)} = \alpha \left( \mathbf{E}^0 e^{ik_z Md} + \frac{1}{d^3 \epsilon} \sum_{m=0}^{N-1} \bar{\bar{F}}_{mM} \cdot \mathbf{p}_{(m,0)} \right), \quad M = 0,1, \ldots, N-1. \tag{43}$$

Since the distribution dyadic $\bar{\bar{f}}_m$ does not depend on $\mathbf{E}_0$, we can choose

$$\mathbf{E}^0 = \mathbf{y}_0 \tag{44}$$

for the case of $E$-polarization incidence and

$$\mathbf{E}^0 = (k_z/k_0)\mathbf{x}_0 + (k_x/k_0)\mathbf{z}_0 \tag{45}$$

for the case of $H$-polarization incidence. Equation (43) can then be written in the following form,

$$\sum_{m=0}^{N-1} \left[ \bar{\bar{I}} \delta_{mM} - \frac{1}{d^3 \epsilon} \alpha \bar{\bar{F}}_{mM} \right] \cdot \mathbf{p}_{(m,0)} = \alpha \mathbf{E}^0 e^{ik_z Md}, \quad M = 0,1,2, \ldots, N-1, \tag{46}$$

where $\delta_{mM}$ is Kronnecker's delta symbol.

The results for the $E$-polarization case then give the $yy$ component of the locality factor $\bar{\bar{L}}_M$ for the $M$th layer according to Eq. (30). In the $H$-polarization case the dipole moment cannot be directed along the $y$ axis, and all the dyadics ($\bar{\bar{F}}_{mM}$, $\bar{\bar{f}}_m$, and $\bar{\bar{L}}_M$) become $2 \times 2$ dyadics. Thus, in this case one determines $xx$, $zx$, $xz$, and $zz$ components of the locality factor, susceptibility, and permittivity according to Eqs. (30), (31), and (19). The $xz$ and $zx$ components in these dyadics should vanish in the static case if the particles are symmetric. They may be significant only when the frequency is quite high. The $xz$ and $zx$ components of the dyadics ($\bar{\bar{L}}_M$, $\bar{\bar{\kappa}}_{loc}$, $\bar{\bar{\epsilon}}_{loc}$) must be equal due to the reciprocity.

If the polarizability of a particle is frequency independent, the frequency dependence of the locality factor $\bar{\bar{L}}_M$ on the wave number $k_0 = \omega\sqrt{\epsilon_0 \mu_0}$ reflects the spatial dispersion effect of the thin film. If the locality factor strongly depends on $k_x/k=\cos\theta$, it means that the spatial dispersion is so strong that the local permittivity loses the physical meaning. In the harmonic case the local permittivity is a dyadic even the particles are isotropic. Using the above approach, we have also validated the prediction of the macroscopic theory for the Brewster angle in Appendix C.

### B. Continuous model for the local permittivity

Like the static case, one can obtain a continuous profile for the local permittivity through computing numerically the averaged field and polarization. The true field can be written in the following form:

$$\mathbf{E}(x,y,z)=\mathbf{E}^{inc}(x,y,z)+\sum_{m=0}^{N-1}\mathbf{E}^{(m)}(x,y,z)+\mathbf{E}^{in}(x,y,z)$$
$$\equiv\mathbf{E}^{inc}(x,y,z)+\mathbf{E}^{dip}(x,y,z)+\mathbf{E}^{in}(x,y,z),$$

where $\mathbf{E}^{(m)}$ is the field produced by the $m$th layer of dipoles, $\mathbf{E}^{dip}(x,y,z)$ is the field produced by all $N$ layers of dipoles [i.e., $\mathbf{E}^{dip}(x,y,z)=\Sigma_{m=0}^{N-1}\mathbf{E}^{(m)}(x,y,z)$], and the term $\mathbf{E}^{in}(x,y,z)$ is the remaining term, which is identically zero outside the particles but nonzero inside the particles.

We choose the case when the particles are dielectric spheres (with radius $b=a/2$) as an example to illustrate the procedure. We average the field $\mathbf{E}(x,y,z)$ over the volume $d\times d\times d$. The sphere radius is assumed to be small compared to the wavelength and thus for the field inside the particle we can apply the Rayleigh relation (20). We can directly calculate the averaged polarization $\langle\mathbf{P}(x,y,z)\rangle$ and the averaged field $\langle\mathbf{E}(x,y,z)\rangle$ at an arbitrary point using definitions (5) and (4). The permittivity $\bar{\bar{\epsilon}}_{loc}(z)$ is then obtained from the following formula [cf. Eqs. (17) and (19)]:

$$\bar{\bar{\epsilon}}_{loc}(z)=\frac{1}{\langle\mathbf{E}\rangle(0,0,z)\cdot\langle\mathbf{E}\rangle(0,0,z)}\langle\mathbf{P}\rangle(0,0,z)\langle\mathbf{E}\rangle(0,0,z)+\epsilon\bar{\bar{I}}. \tag{47}$$

After the dipole moments $\mathbf{p}_{(m,0)}$, $m=0,1,\dots,N-1$, are computed by solving the system (46), one can find the continuous functions $\langle\mathbf{P}\rangle(0,0,z)$ and $\langle\mathbf{E}\rangle(0,0,z)$ as follows. Like the true field, the averaged field $\langle\mathbf{E}\rangle(0,0,z)$ can be separated into the following three parts:

$$\langle\mathbf{E}\rangle(0,0,z)=\langle\mathbf{E}^{inc}\rangle(0,0,z)+\langle\mathbf{E}^{dip}\rangle(0,0,z)+\langle\mathbf{E}^{in}(0,0,z)\rangle. \tag{48}$$

It is shown in Appendix D that

$$\langle\mathbf{E}^{inc}\rangle(0,0,z)=\left(\frac{\sin(k_xd/2)}{(k_xd/2)}\right)\left(\frac{\sin(k_zd/2)}{(k_zd/2)}\right)e^{ik_zz}\mathbf{E}^0, \tag{49}$$

$$\langle\mathbf{E}^{dip}\rangle(0,0,z)=\sum_{m=0}^{N-1}\left[\frac{\bar{\bar{G}}_m(z)}{\epsilon d^3}\cdot\mathbf{p}_{(m,0)}\right], \tag{50}$$

where

$$\bar{\bar{G}}_m(z)=\sum_{l=-\infty}^{+\infty}\frac{(-1)^l}{2k_z^{(l)}d}\left(\frac{\sin(k_xd/2)}{(k_xd/2+l\pi)}\right)\bar{\bar{S}}^{(l)}W_m^{(l)}(z), \tag{51}$$

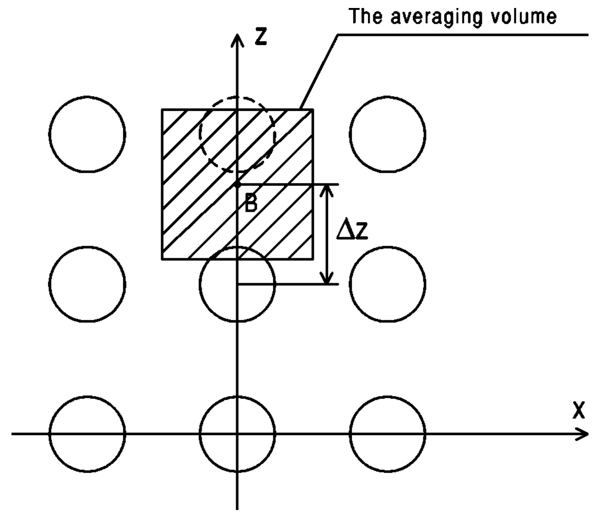


FIG. 2. Geometry for the averaging.

$$\bar{\bar{S}}^{(l)}=(k_z^{(l)}d)^2\mathbf{x}_0\mathbf{x}_0+[(k_z^{(l)}d)^2-(k_x^{(l)}d)^2]\mathbf{y}_0\mathbf{y}_0-(k_x^{(l)}d)^2\mathbf{z}_0\mathbf{z}_0$$
$$+(\mathbf{x}_0\mathbf{z}_0+\mathbf{z}_0\mathbf{x}_0)(ik_z^{(l)}d)(k_x^{(l)}d),$$

and where the function $W_m^{(l)}(z)$ has the following expression

$$W_m^{(l)}(z)=\frac{2-e^{k_z^{(l)}(|z-md|-d/2)}-e^{-k_z^{(l)}d}}{k_z^{(l)}d} \tag{52}$$

for the case $|z-md|<d/2$, and

$$W_m^{(l)}(z)=\left(\frac{\sinh(k_z^{(l)}d/2)}{k_z^{(l)}d/2}\right)e^{-k_z^{(l)}|z-md|} \tag{53}$$

for the case $|z-md|>d/2$. Here $k_z^{(l)}=\sqrt{(k_x+2\pi l/d)^2-k^2}$ and for $l=0$ one has $k_z^{(0)}=ik_z$.

Consider a spherical particle (with radius $b$) at the $M$th layer. Introduce the following notation:

$$\mathbf{E}^M=-\frac{\mathbf{p}_{(M,0)}}{3\epsilon V_0}, \tag{54}$$

$$V_0=\frac{4\pi b^3}{3}. \tag{55}$$

Denote $\Delta z\equiv z-Md$. If $\Delta z$ is in the interval $[d/2,d/2+b]$, the volume of the sphere part inside the averaging volume $d^3$ is (see Fig. 2)

$$V_1=\frac{\pi}{6}(b+d/2-\Delta z)[3b^2+3(d/2-\Delta z)^2$$
$$+(b+d/2-\Delta z)^2].$$

For $d/2-b\leq\Delta z\leq d/2$, the volume of the sphere part inside the averaging volume $d^3$ is

$$V_1=V_0-\frac{\pi}{6}(b-d/2+\Delta z)[3b^2+3(d/2-\Delta z)^2$$
$$+(b-d/2+\Delta z)^2].$$

Averaging $\mathbf{P}$ and $\mathbf{E}^{in}$ at each point over its associated averaging volume, one can easily obtain the following results

(i) for $(M-\frac{1}{2})d+b \leqslant z \leqslant (M+\frac{1}{2})d-b$, $M=0,\ldots,N-1$,

$$\langle \mathbf{P}\rangle(0,0,z)=\mathbf{p}_{(M,0)}/d^3, \tag{56}$$

$$\langle \mathbf{E}^{in}\rangle(0,0,z)=\mathbf{E}^M V_0/d^3; \tag{57}$$

(ii) for $(M+\frac{1}{2})d-b \leqslant z \leqslant (M+\frac{1}{2})d+b$, $M=0,\ldots,N-2$,

$$\langle \mathbf{P}\rangle(0,0,z)=\mathbf{p}_{(M,0)}\frac{V_1}{d^3V_0}+\mathbf{p}_{(M+1,0)}\frac{V_0-V_1}{d^3V_0}, \tag{58}$$

$$\langle \mathbf{E}^{in}\rangle(0,0,z)=\mathbf{E}^M\frac{V_1}{d^3V_0}+\mathbf{E}^{M+1}\frac{V_0-V_1}{d^3V_0}; \tag{59}$$

(iii) for $(M+\frac{1}{2})d-b \leqslant z \leqslant (M+\frac{1}{2})d+b$ with $M=N-1$, or $(M-\frac{1}{2})d-b \leqslant z \leqslant (M-\frac{1}{2})d+b$ with $M=0$,

$$\langle \mathbf{P}\rangle(0,0,z)=\mathbf{p}_{(M,0)}V_1/V_0d^3, \tag{60}$$

$$\langle \mathbf{E}^{in}\rangle(0,0,z)=\mathbf{E}^M V_1/d^3; \tag{61}$$

(iv) for $z \leqslant -d/2-b$ or $z \geqslant (N-1/2)d+b$,

$$\langle \mathbf{P}\rangle(0,0,z)=\langle \mathbf{E}^{in}\rangle(0,0,z)=0. \tag{62}$$

The formulas presented in this subsection give a quite explicit and accurate approach for computing the local permittivity of the thin film as a continuous function of the depth $z$.

### C. Numerical results

As a numerical example, we consider the dielectric spheres (with radius $b$) in vacuum, i.e., $\epsilon=\epsilon_0$. The permittivity for the inclusion particles is chosen to be $\epsilon_p=10\epsilon_0$. The polarizability of the dielectric spheres is given by the following formula (see, e.g., Ref. 19),

$$\alpha=4\pi\epsilon b^3\frac{\epsilon_p-\epsilon}{\epsilon_p+2\epsilon}.$$

We choose $b=d/4$ in our numerical example. The total number of layers in the thin film is $N=4$. In the calculation of the interaction tensor $\bar{\bar{F}}_{mM}$, the series in Eqs. (34)–(37) converge very rapidly and thus we take $l_1=l_2=4$. In the discrete model, the relative permittivity tensor $\bar{\bar{\epsilon}}_r=\bar{\bar{\epsilon}}_{loc}/\epsilon_0$ for each layer is computed by using Eqs. (31) and (19). For the $E$-polarization case, the $yy$ component of $\bar{\bar{\epsilon}}_r$ for each layer is computed and plotted in Fig. 3(a) as a function of the incident angle $\theta$. The $xx$ and $zz$ components of the tensor $\bar{\bar{\epsilon}}_r$ for each layer are determined from the $H$-polarization case and are plotted in Figs. 3(b) and 3(c) as functions of the incident angle. Note that the tensor $\bar{\bar{f}}_M$ for the $H$-polarization case is quite singular and we find the tensor $\bar{\bar{L}}_M$ from expression (30) (which contains the inversion of $\bar{\bar{f}}_M$) using the singular value decomposition method (see, e.g., Ref. 20). As one can see from Figs. 3(a)–3(c), the permittivity is practically independent of the incident angle for $kd=0.1$ and $kd=0.2$ and depends weakly on the incident angle for $kd=0.5$. Our numerical results indicate that for $kd \leqslant 10^{-3}$ the variation in the dipole moments from one layer to another does not exceed 0.2%, which is consistent with the results obtained by Ewald in Ref. 21 and Sivukhin in Ref. 14 for the static case. In the quasistatic case $kd \leqslant 0.1$, the difference between the relative permittivity obtained by the Lorentz formula (which gives

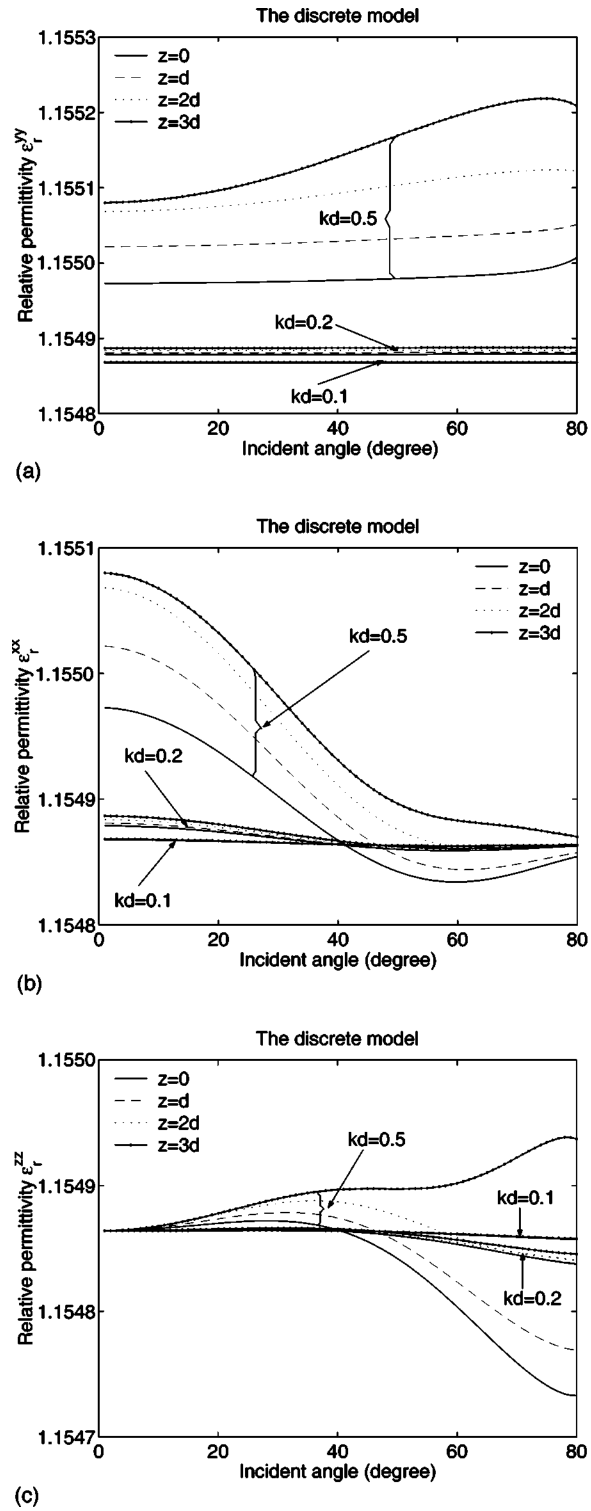


FIG. 3. Components of the relative permittivity tensor (obtained from the discrete model for a four-layered thin film) as functions of the incident angle.

$\epsilon_r = 1.15487$) and the one obtained by our discrete formulas does not exceed $10^{-3}$ (see Fig. 3).

For the continuous model, the $yy$ component (for the $E$-polarization case) and $xx$ and $zz$ components (for the $H$-polarization case) of the relative permittivity tensor $\bar{\bar{\epsilon}}_r$ are calculated and presented as functions of the vertical coordinate $z$ in Figs. 4(a)–4(c), respectively, for $kd = 10^{-3}$ and $\theta = 45°$ (the dependence of $\bar{\bar{\epsilon}}_r$ on the incident angle $\theta$ is very weak for $kd \leqslant 1$). As one can see from Fig. 4, the components of the relative permittivity tensor have a transition zone around each surface of the thin film and the thickness of the transition zone is approximately equal to the particle size $a = 2b = d/2$. As a validation of our models, the local permittivity obtained by the discrete model and the continuous model are in a very good agreement for relatively low frequencies $kd \leqslant 0.5$.

For these frequencies we have also compared the coordinate-independent effective permittivity obtained by Eq. (16) with that obtained from Eq. (47) for an $N$-layered slab. This way we find numerically the distance from the surface of the slab where the permittivity is getting almost coincident with that predicted by Lorenz-Lorentz theory. If $N = 4$ for two inner layers the error in the effective permittivity associated with the use of the Lorentz formula does not exceed $10^{-3}$, whereas for the surface layers this error has the order of several percent. Thus, the Lorentz formula can be used for a quite thin slab. We characterize the anisotropicity (due to the surface effects) of the thin film through a so-called anisotropic coefficient, which is defined by

$$\gamma_a = \left| \frac{\epsilon_{eff}^t - \epsilon_{eff}^n}{\epsilon_{eff}^t} \right| .$$

The effective dielectric constants $\epsilon_{eff}^t$ and $\epsilon_{eff}^n$ are calculated from expressions (21) and (22). The local permittivity tensors are calculated from Eqs. (19) and (31). At low frequencies (for $kd \leqslant 0.2$), $\epsilon_{loc}^{yy} \approx \epsilon_{loc}^{xx} \equiv \epsilon_{loc}^t$ for all the incident angles (as can be seen from Fig. 3). This result is expected and can be considered as a check. In the quasistatic case ($kd \leqslant 0.01$) the normal and transverse components of the effective permittivity (for the present four-layered thin film) are approximately equal to 1.1211 and 1.1451, respectively, which correspond to $\gamma_a = 0.0209$ for the anisotropic coefficient. The anisotropic coefficient $\gamma_a$ is in the interval 0.0206–0.0209 for $kd \leqslant 0.2$. The Brewster angle, calculated from formula (C3) in Appendix C, is equal to 47.35° and does not depend on the frequency (for $kd \leqslant 1$). This Brewster angle is quite close to 47.28°, which is the prediction of the macroscopic theory according to formula (C4) [in which we take $\epsilon_{eff} = (\epsilon_{eff}^t + \epsilon_{eff}^n)/2$].

Finally, we present the normal electric field $E_z$ (for the $H$-polarization case) as a function of the depth $z$ in Fig. 5. As one can see from this figure, the normal electric field has a similar transition zone as the local permittivity.

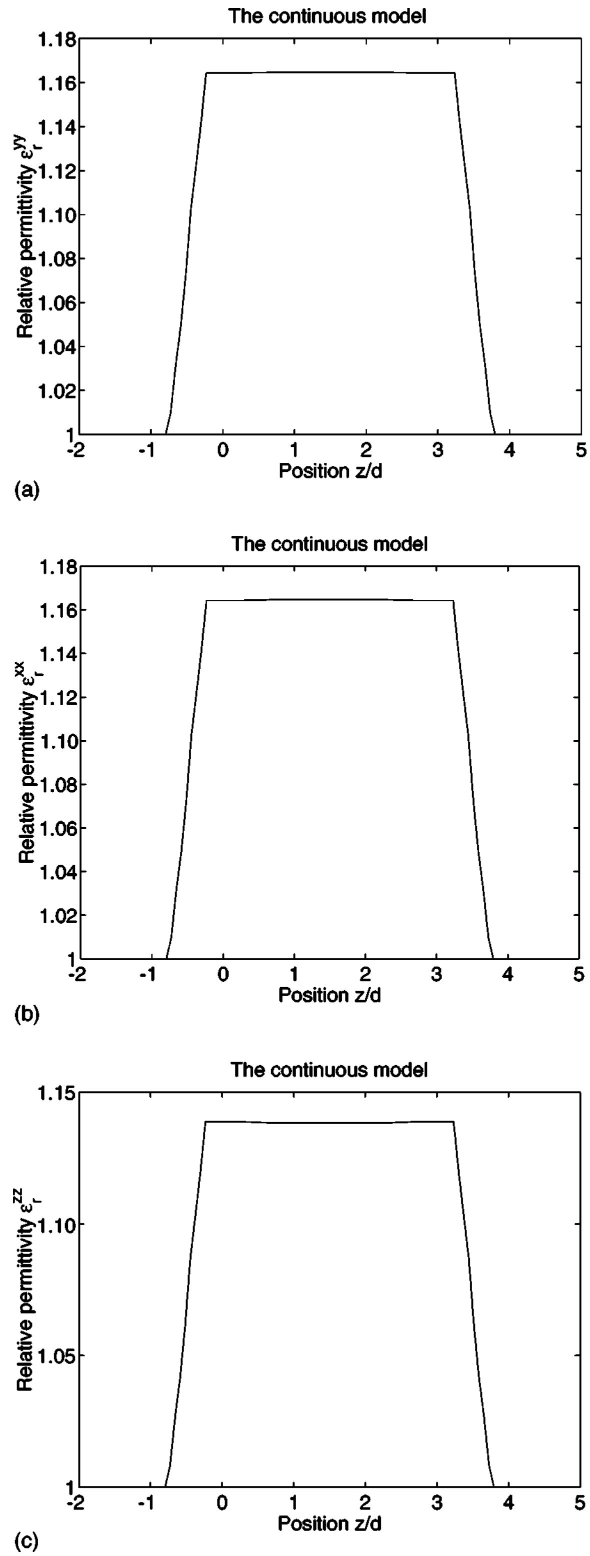


FIG. 4. Components of the relative permittivity tensor (obtained from the continuous model for a four-layered thin film) as functions of the vertical position $z$.

## IV. CONCLUSION

In the present paper, we have presented an accurate model for the dielectric properties of a thin film consisting a few layers of particles (or molecules) for both the static and harmonic cases. Even for the case of isotropic particles, the local permittivity becomes uniaxial near the two surfaces of the thin film. The depth dependence and the anisotropic behavior of the local permittivity due to the surface environ-

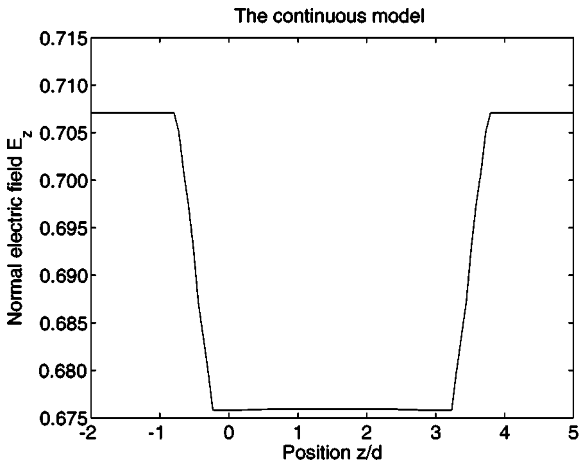


FIG. 5. The distribution of the normal component of the electric field obtained from the continuous model for the $H$-polarization case.

ment are studied both analytically and numerically. The coefficient of the anisotropy is of the order of several percent. The thin film can be described accurately as a slab of continuous medium if the frequency is low enough ($kd<0.5$, where $d$ is the distance between two neighboring particles). In the harmonic case, the nonuniform distribution of the field and polarization has been taken into account not only near the surfaces, but also inside the thin film. We have developed two different models for the computation of the local permittivity, namely, the discrete model and the continuous model. For the local permittivity at low frequencies ($kd<0.5$), both models give consistent results, which are very close to those obtained in the framework of the Lorentz-Clausius-Mossotti approximation. Numerical results have shown that the depth for the transition zone (in which the permittivity varies significantly) near a surface is about the particle size. Numerical results have also shown that the Brewster angle for such a thin film coincides with the prediction of the macroscopic theory. The detailed derivation has been carried out using the dipole approximation for the field interactions of particles with the assumption that the array of particles are sparse. The method can be easily extended to include higher-order multipoles when the array of particles are dense.

## ACKNOWLEDGMENTS

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## APPENDIX A: ERROR ESTIMATE FOR THE LORENTZ FORMULA FOR A THIN FILM CONSISTING OF A SINGLE LAYER OF PARTICLES

As an approximation, the Lorentz formula (16) for the static case has the maximal error when the composite slab consists only one layer of particles. In this appendix, we estimate this maximal error. We apply the theorem of Kontorovich *et al.*[22] in which the averaged field of discrete sources equals the true field of the averaged sources if the rule of averaging is the same.

Consider first the case when the induced dipoles are horizontally oriented at the plane of the particle array. Subtracting the external field from the local field, one obtains the *interaction field* $\mathbf{E}^{int}$ defined as the contribution of the polarized structure to the local field. The relation between this field and the dipole moment $\mathbf{p}$ is[23]

$$\mathbf{E}^{int}=C\mathbf{p}/\epsilon,$$

where $C$ is a constant. For a square array of horizontal dipoles, $C$ has the following value [see Eq. (12.27) of Ref. 23],

$$C=\frac{1.2-8\pi^2K_0(2\pi)}{\pi d^3}\approx 0.359/d^3, \qquad \text{(A1)}$$

where $K_0$ is MacDonald's function. On the other hand, the Lorentz formula (16) gives $C=0.33/d^3$ for this case. Thus, the relative error for using the Lorentz formula (16) for this case is about $(0.359-0.33)/0.359=8\%$.

Next we consider the case when the induced dipoles are vertically oriented (i.e., $z$-directed) at the plane of the particle array. Using the theorem of Kontorovich *et al.* it can easily be shown that the field averaged over the cubic cell $d\times d\times d$ centered at the plane of the particle array equals the field inside the slab of continuous volume polarization $\mathbf{P}=\mathbf{p}/d^3$. Thus, one has

$$\mathbf{E}^{av}=-\frac{\mathbf{P}}{\epsilon}+\mathbf{E}^{ext}.$$

It follows from Collin's notation that

$$\mathbf{E}^{loc}-\mathbf{E}^{av}=\frac{\mathbf{P}}{\epsilon}+\frac{Cd^3\mathbf{P}}{\epsilon}.$$

For a square array of vertical dipoles, $C$ has the following value [see Eq. (12.30) of Ref. 23],

$$C=\frac{-2.4+16\pi^2K_0(2\pi)}{\pi d^3}\approx -0.7187/d^3. \qquad \text{(A2)}$$

On the other hand, the Lorentz formula (16) gives $C=-0.66/d^3$ for this case. Thus, the relative error for using the Lorentz formula (16) for this case is about $(0.7187-0.6666)/0.7187=8\%$. Therefore, the maximal error of our method for the static case is about 8%, which takes place in the limiting case when the slab consists only of a single layer of particles.

## APPENDIX B: THE INTERACTION DYADIC

In this Appendix, we derive the explicit expression for the interaction dyadic $\bar{\bar{F}}_{mM}$. Consider first the case when $m\neq M$. Then the point $(x=y=0,\ z=Md)$ where the field is calculated does not belong to the $m$ layer, which produces the field. The vector potential at the point $(x,y,z)$ produced by all the particles of the $m$th layer can be written as follows,

$$\mathbf{A}^{(m)}=\frac{k}{4\pi\sqrt{\epsilon\mu_0}}\mathbf{p}_{(m,0)}\sum_{l_1,l_2=-\infty}^{+\infty}\frac{\exp[-i(kR_l+k_xdl_1)]}{R_l}$$

$$=\frac{-ik}{2d^2\sqrt{\epsilon\mu_0}}\mathbf{p}_{(m,0)}\sum_{l_1,l_2=-\infty}^{+\infty}\frac{\exp\left\{-i\left[|z-md|Q_l+\left(k_x+\frac{2\pi l_1}{d}\right)x+\left(\frac{2\pi l_2}{d}\right)y\right]\right\}}{Q_l},$$

where

$$R_l=\sqrt{(dl_1-x)^2+(dl_2-y)^2+z^2},$$

$$Q_l=\sqrt{k^2-\left(k_x+\frac{2\pi l_1}{d}\right)^2-\left(\frac{2\pi l_2}{d}\right)^2}.$$

This representation of vector potential is the well-known Floquet's expansion for the field produced by a regular dipolar array in terms of spatial harmonics.[24] It can be written in a more convenient way as follows,

$$\mathbf{A}^{(m)}=\frac{k}{2d^2\epsilon}\mathbf{p}_{(m,0)}\sum_{l_1,l_2=-\infty}^{+\infty}\frac{e^{(-|z-md|k_z^{(l)}-ik_x^{(l)}x-ik_y^{(l)}y)}}{k_z^{(l)}},$$

where

$$k_x^{(l)}=k_x+\frac{2\pi l_1}{d},\quad k_y^{(l)}=\frac{2\pi l_2}{d},\quad k_z^{(l)}=\sqrt{k_x^{(l)2}+k_y^{(l)2}-k^2}.$$

The corresponding electric field can be found from the following Lorentz gauge,

$$\mathbf{E}^{(m)}=\frac{i\eta}{k}\nabla\times(\nabla\times\mathbf{A}^{(m)}),$$

where $\eta=\sqrt{\mu_0/\epsilon}$. The above formula can be written in the following explicit matrix form,

$$\mathbf{E}^{(m)}=\frac{1}{2d^2\epsilon}\sum_{l_1,l_2=-\infty}^{+\infty}\frac{e^{(-|z-md|k_z^{(l)}-ik_x^{(l)}x-ik_y^{(l)}y)}}{k_z^{(l)}}\begin{pmatrix}(k_z^{(l)})^2-(k_y^{(l)})^2 & k_x^{(l)}k_y^{(l)} & ik_x^{(l)}k_z^{(l)}\\ k_x^{(l)}k_y^{(l)} & (k_z^{(l)})^2-(k_x^{(l)})^2 & ik_y^{(l)}k_z^{(l)}\\ ik_x^{(l)}k_z^{(l)} & ik_y^{(l)}k_z^{(l)} & -(k_x^{(l)})^2-(k_y^{(l)})^2\end{pmatrix}\mathbf{p}_{(m,0)}. \tag{B1}$$

Thus, one obtains the following expression for this field at the point $(x=y=0,\ z=Md)$,

$$\mathbf{E}^{(Mm)}=\frac{1}{2d^3\epsilon}\sum_{l_{1,2}=-\infty}^{+\infty}\frac{e^{-|M-m|dk_z^{(l)}}}{k_z^{(l)}d}\begin{pmatrix}(k_z^{(l)}d)^2-(k_y^{(l)}d)^2 & k_x^{(l)}k_y^{(l)}d^2 & ik_x^{(l)}k_z^{(l)}d^2\\ k_x^{(l)}k_y^{(l)}d^2 & (k_z^{(l)}d)^2-(k_x^{(l)}d)^2 & ik_y^{(l)}k_z^{(l)}d^2\\ ik_x^{(l)}k_z^{(l)}d^2 & ik_y^{(l)}k_z^{(l)}d^2 & -(k_x^{(l)}d)^2-(k_y^{(l)}d)^2\end{pmatrix}\mathbf{p}_{(m,0)}\equiv\frac{1}{d^3\epsilon}\bar{\bar{F}}_{mM}\cdot\mathbf{p}_{(m,0)}. \tag{B2}$$

The dyadic $\bar{\bar{F}}_{mM}$ (for $m\neq M$) defined above leads to Eqs. (32) and (33). Note that all the series in the expression for $\bar{\bar{F}}_{mM}$ $(m\neq M)$ converge well and the high-order terms decrease exponentially as $l_1$ and $l_2$ increase.

Next we want to derive the field at the point $(x=y=0,\ z=Md)$ produced by the particles in the $M$th layer except the 0-numbered particle of this layer (i.e., the particle which contains the field point). This is the so-called *interaction field* of a 2D regular square array. This interaction field has been studied for horizontal dipoles in Ref. 23, for vertical dipoles in Ref. 25, and for the general case of arbitrarily oriented dipoles in Ref. 26. In particular, if the grating period is so small that $kd\leqslant 0.2$ the interaction field produced by the planar array of dipoles (horizontal or vertical) can be considered as approximately static for incident angles less than 80°. We will only consider these incident angles and thus the dyadic $\bar{\bar{F}}_{MM}$ is diagonal. The components of the interaction dyadic for the static case are[23]

$$F_{MM}^{xx,yy}=0.359,\quad F_{MM}^{zz}=-0.718.$$

If the incidence is very oblique (more than 80°), one has to consider the high-frequency corrections even for a small $kd$, and use very complicated formulas given in Refs. 26, 25, and 23. This case is not interesting for our purposes.

## APPENDIX C: THE BREWSTER FUNCTION

The field reradiated in the reflection direction (making an angle $\theta$ with the vertical axis; see Fig. 1) by a layer of dipoles is proportional to the transverse (with respect to this reflection direction) component of the dipole moment, since the longitudinal component of the dipole moment does not contribute to this field. Therefore, the complex amplitude of the field reradiated by the $M$th layer can be written in the following form,

$$E_M=A(\theta)(p_{Mx}\cos\theta+p_{Mz}\sin\theta),$$

where $\mathbf{p}_M$ is the dipole moment for the 0-numbered dipole of this layer [other dipoles at this layer are expressed in terms of the 0-numbered dipole by Eq. (27)]. Consequently, the complex amplitude of the field reflected by the thin film can be written as follows:

$$E^r = A(\theta)\sum_{M=0}^{N-1} e^{-iMkd\cos\theta}(p_{Mx}\cos\theta + p_{Mz}\sin\theta). \qquad (C1)$$

One can rewrite the above equation in the following form,

$$E^r = A(\theta)(S_x\cos\theta + S_z\sin\theta), \qquad (C2)$$

where

$$S_x = \sum_{M=0}^{N-1} e^{-iMkd\cos\theta}p_{Mx}, \quad S_z = \sum_{M=0}^{N-1} e^{-iMkd\cos\theta}p_{Mz}.$$

Averaging $E^r$ over the temporal period $2\pi/\omega$ and dividing expression (C2) by a factor $|A(\theta)\hat{S}_z\cos\theta|$, one obtains the following normalized angular dependence of the reflection coefficient,

$$f_{Br}(\theta) \equiv \frac{\hat{E}^r}{|A(\theta)\hat{S}_z\cos\theta|} = \left|\frac{|S_x|}{|S_z|}\cos(\phi_x - \phi_z) - \tan\theta\right|, \qquad (C3)$$

where the caret denotes temporal averaging, and $\phi_x$ and $\phi_z$ are the phases of the complex values $S_x$ and $S_z$, respectively. Function $f_{Br}(\theta)$ is called the *Brewster function*, since the reflected filed $E^r = 0$ when $f_{Br}(\theta) = 0$. The zero of the Brewster function $f_{Br}(\theta)$ is Brewster's angle. Note that in the macroscopic theory the condition for Brewster's angle is (see, e.g., Ref. 27)

$$\tan\theta_{Br} = \sqrt{\epsilon_{eff}}. \qquad (C4)$$

## APPENDIX D: THE AVERAGED FIELD

Consider expression (B1), which gives the field at an arbitrary point produced by the $m$th layer of particles. Adding these fields for all layers and taking the average in accordance with Eq. (4), one obtains the following averaged dipolar field $\langle \mathbf{E}^{dip}\rangle$,

$$\langle \mathbf{E}^{dip}\rangle(\mathbf{r}) = \frac{1}{d^3}\sum_{m=0}^{N-1}\int_{x-d/2}^{x+d/2}\int_{y-d/2}^{y+d/2}\int_{z-d/2}^{z+d/2}\mathbf{E}^{(m)}d^3\mathbf{r}'. \qquad (D1)$$

When integrating along the $y$ axis over the interval $[y-d/2, y+d/2]$, all the terms with $k_y^{(l)}$ [cf. Eq. (B1)] vanish except the term with $l_2 = 0$ (and thus $k_y^{(l)} = 0$). Then one can renumerate the series in Eq. (B1) with $l_1 = l$, $l_2 = 0$. Integration of $\exp(-ik_x^{(l)}x)$ along the $x$ axis gives the following factor,

$$\left(\frac{\sin(k_x d/2)}{k_x d/2 + l\pi}\right),$$

and the integration of $\exp(-ik_y y)$ along the $y$ axis gives the factor

$$\left(\frac{\sin(k_y d/2)}{k_y d/2}\right).$$

The integration of $\exp(-k_z^{(l)}|z-md|)$ along the $z$ axis can be made separately for the case $|z-md| \leqslant d/2$ and the case $|z-md| \geqslant d/2$. In the first case,

$$\frac{1}{d}\int_{z-d/2}^{z+d/2}\exp(-k_z^{(l)}|z'-md|)dz' = W_m^{(l)}(z),$$

where $W_m^{(l)}(z)$ is given by Eq. (52). In the second case, the above integration equals $W_m^{(l)}(z)$ given by Eq. (53). Finally, we obtain expression (50) for the averaged dipolar field. In a similar way, one can obtain expression (49) for the averaged incident field. Note that the series in expression (B1) for the dipolar field is divergent when $z = md$ and therefore we should remove an infinitesimal region around the point with $z = md$ in the averaging integration (i.e., the volume averaging integral is understood as its principal value).

To average the field $\mathbf{E}^{in}$ over the volume of the 0-numbered particle at the $M$th layer, we notice that

$$\mathbf{E}^{in} = \mathbf{E}^{(p)} - \mathbf{E}^{int} - \mathbf{E}_M^{dip} - \mathbf{E}^{inc},$$

where $\mathbf{E}^{(p)}$ is the total field inside the particle, $\mathbf{E}_M^{dip}$ is the field produced by the reference particle (i.e., the 0-numbered particle at the $M$th layer), the interaction field $\mathbf{E}^{int}$ is the field produced by all the particles except the reference particle, and $\mathbf{E}^{inc} = \mathbf{E}_0 e^{-ik_z Md}$ is the incident field. Since $\langle \mathbf{E}_M\rangle = 0$ (i.e., the principal value of the volume integration over a sphere of the field produced by a dipole located at the center of the sphere is zero) and $\mathbf{E}^{int} = \mathbf{E}^{loc} - \mathbf{E}^{inc}$, one obtains

$$\langle \mathbf{E}^{in}\rangle = \mathbf{E}^{(p)} - \langle \mathbf{E}^{loc}\rangle.$$

Using the Rayleigh relation (20) and the above equation, one obtains the expressions (57) and (54).


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