PHYSICAL REVIEW B VOLUME 32, NUMBER 8 15 OCTOBER 1985

Electromagnetic response of systems with spatial fluctuations. II. Applications

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(Received 3 July 1984; revised manuscript received 8 February 1985)

A general formalism for the calculation of the macroscopic dielectric response of spatially fluctuating systems is used to obtain, following a unified approach, expressions for (1) the corrections to the Clausius-Mossotti dielectric function in disordered systems, (2) the optical coefficients and the surface plasmon polaritons of rough surfaces, (3) the electromagnetic modes of infinite crystals, and (4) the change in the macroscopic dielectric response of a crystal in the neighborhood of its surface, under the assumption that the length scale of the fluctuations is much smaller than the wavelength of light.

I. INTRODUCTION

In the preceding paper[1] we have obtained closed-form expressions for the macroscopic dielectric response of systems with microscopic spatial fluctuations in terms of their microscopic dielectric operator, taking into account the local-field effect and using very relaxed assumptions. In this paper we take advantage of the generality of these expressions in order to calculate the dielectric and optical properties of several systems of very diverse nature following a unified approach. These systems are a disordered medium, such as a liquid, made of point-polarizable atoms, the rough surface, and the infinite and semi-infinite crystal. Our aim is to clarify through definite examples the meaning and usage of the representation-free, average-free formulas obtained in Ref. 1, to demonstrate their correctness by obtaining from them well-known results, to get some new results, and ultimately, to gain insight about the underlying structure of the macroscopic response of spatially fluctuating systems.

The simplest theory of the local-field effects is the Clausius-Mossotti theory of the macroscopic dielectric response of a cubic crystal of point-polarizable atoms in terms of their atomic polarizability.[2] This model of point-polarizable atoms has also been applied to noncubic crystals and glasses.[3] The calculation of the longitudinal macroscopic dielectric response of crystals from more realistic quantum-mechanical microscopic models was pioneered by Adler[4] and Wiser,[5] using the random-phase-approximation[6] (RPA) expressions for the microscopic response. Many calculations of this kind were made afterwards,[7–11] some with special emphasis on noncubic crystals[12] and on the transverse response.[13]

There have been relatively few calculations that take into account the surface of the crystal. Some take into account the surface electronic band structure but ignore the surface local-field effect.[14,15] Others consider the local-field effect in the neighborhood of the surface, but do so within the point-charge[16] or point-polarizable-atom approximation.[17–21] Some more elaborate calculations that use a more realistic microscopic response have been done recently.[22–24]

Other physical systems where the local-field effect has been considered important are the liquid and the disordered composite medium, made of small polarizable entities. Using the classical method of the Lorentz cavity,[25] we obtain the Clausius-Mossotti relation between the macroscopic dielectric function and the polarizability, assuming that the microscopic electric field produced by the near molecules adds up to zero. That this is not so in liquids was pointed out by Kirkwood[26] and Yvon,[27] who calculated the corrections to the Clausius-Mossotti dielectric function to lowest order in the polarizability for a plane-condenser geometry. Several expressions have been obtained thereafter for the macroscopic dielectric response of nonpolar polarizable liquids of low[28–30] and moderate[31–33] densities.

A problem closely related to that of the liquid is the calculation of the effective dielectric function of a composite medium composed of small particles embedded in a dielectric host. The usual theory for this system was developed by Maxwell-Garnett,[34] based on the Clausius-Mossotti relation. The ambiguity between host and embedded particles at high densities was later resolved by Bruggeman[35] with his symmetric effective-medium theory. Only lately have the effects of disorder been taken into account[36] within the coherent-potential approximation.

Finally we mention another class of systems where spatial fluctuations play an important role: the rough surfaces. The optical properties of these systems were first calculated by Fano[37] by adapting the scalar theory of diffraction by gratings developed earlier by Rayleigh.[38] Several approaches have been used in past calculations of these optical properties. One of them consists of imposing boundary conditions on the electromagnetic field at the actual rough surface and then making an expansion of these in powers of the surface height above a nominal flat surface.[39–41] Another consists of replacing the rough surface by a distribution of singular surface currents on a plane surface.[42,43] Still another consists of making a coordinate transformation such that the rough surface becomes planar in the new coordinate system, and afterwards imposing boundary conditions at this plane sur-

face.[44] A different approach is the solution of an integral equation obtained from the extinction theorem.[45] The equivalence between the boundary-condition and surface-current approaches has been shown by Kröger and Kretschmann,[46] and the relationship of these approaches to the extinction-theorem approach has been discussed by Toigo, Marvin, Celli, and Hill[47] for the case of local media. If the media are spatially dispersive, the previous approaches, with exception of the extinction-theorem one,[48,49] are not applicable. Recently the semiclassical infinite-barrier approximation has been extended in order to handle rough nonlocal metallic surfaces.[50] To our knowledge, the relationship between the optical properties of rough surfaces and the local-field effect has not been considered before the present paper.

The main purpose of this paper is to show how the dielectric response and the optical properties of systems as diverse as those discussed above, but which have in common the presence of spatial fluctuations, can be calculated using the general theory of the local-field effect we developed in Ref. 1. For convenience, we summarize the main results of that theory in the following equations, valid when the fluctuation length scale is much less than the free-space wavelength of light:

$$\hat{\epsilon}_M = \hat{\epsilon}_{aa} - \hat{\epsilon}_{af}(\hat{\epsilon}_{ff}^{\mathrm{LL}})^{-1}\epsilon_{fa} , \tag{1}$$

$$\hat{\epsilon}_M^{-1} = (\hat{\epsilon}^{-1})_{aa} - (\hat{\epsilon}^{-1})_{af}[(\hat{\epsilon}^{-1})_{ff}^{\mathrm{TT}}]^{-1}(\hat{\epsilon}^{-1})_{fa} , \tag{2}$$

$$\begin{aligned}(\hat{\epsilon}_M^{\mathrm{LL}})^{-1} &= (\hat{\epsilon}^{\mathrm{LL}})_{aa}^{-1} \\ &= \hat{\nabla}\hat{\nabla}^{-2}(\hat{\epsilon}^{\mathrm{cc}})_{aa}^{-1}\hat{\nabla} \\ &= \hat{\nabla}(\hat{\epsilon}^{\phi\phi})_{aa}^{-1}\hat{\nabla}^{-2}\hat{\nabla} ,\end{aligned} \tag{3}$$

$$[(\hat{\epsilon}_M^{-1})^{\mathrm{TT}}]^{-1} = [(\hat{\epsilon}^{-1})^{\mathrm{TT}}]_{aa}^{-1} , \tag{4}$$

where $\hat{\epsilon}$ is the microscopic and $\hat{\epsilon}_M$ the macroscopic dielectric operators (L and T represent longitudinal and transverse projections, respectively), $\hat{\nabla}$ and $\hat{\nabla}^{-2}$ are the gradient and inverse Laplacian operators, respectively, and we introduced the notation

$$\begin{aligned}&\hat{O}^{AB} = \hat{P}^A\hat{O}\hat{P}^B, \quad A,B = \mathrm{L},\mathrm{T} \\ &\hat{O}_{\alpha\beta} = \hat{P}_\alpha\hat{O}\hat{P}_\beta, \quad \alpha,\beta = a,f\end{aligned} \tag{5}$$

for any operator $\hat{O}$. Here, $\hat{P}^{\mathrm{L}}$ and $\hat{P}^{\mathrm{T}}$ are the longitudinal and the transverse projectors, respectively, and $\hat{P}_a$ and $\hat{P}_f$ are projectors that extract the average and the fluctuating parts of the fields, and can be chosen from a large class of projectors as they best fit the system under consideration. We also introduced the external-charge (ρ_{ext}) —total-charge (ρ) density response function $(\hat{\epsilon}^{\mathrm{cc}})^{-1}$, and the external-potential (ϕ_{ext}) —total-potential (ϕ) response function $(\hat{\epsilon}^{\phi\phi})^{-1}$, which obey

$$\rho = (\hat{\epsilon}^{\mathrm{cc}})^{-1}\rho_{\mathrm{ext}} , \tag{6}$$

and

$$\phi = (\hat{\epsilon}^{\phi\phi})^{-1}\phi_{\mathrm{ext}} , \tag{7}$$

in the absence of transverse electric fields. We also recall the interpretation of the inverse longitudinal-longitudinal dielectric response as the external-polarization ($\mathbf{P}_{\mathrm{ext}}$) —electric-field response function,

$$\mathbf{E}^{\mathrm{L}} = -4\pi(\hat{\epsilon}^{\mathrm{LL}})^{-1}\mathbf{P}_{\mathrm{ext}} , \tag{8}$$

in the absence of retardation, and its relation to the transverse-transverse dielectric response:

$$\begin{aligned}[(\hat{\epsilon}^{-1})^{\mathrm{TT}}]^{-1} &= \hat{\epsilon}^{\mathrm{TT}} - \hat{\epsilon}^{\mathrm{TL}}(\hat{\epsilon}^{\mathrm{LL}})^{-1}\hat{\epsilon}^{\mathrm{LT}} \\ &= \hat{\epsilon} - \hat{\epsilon}(\hat{\epsilon}^{\mathrm{LL}})^{-1}\hat{\epsilon} .\end{aligned} \tag{9}$$

The organization of this paper is as follows: In Sec. II we use our general formalism in order to calculate corrections to the Clausius-Mossotti dielectric response for a nonpolar liquid. In Sec. III we calculate the optical coefficients and the surface plasmon-polariton dispersion relation for a medium bounded by a rough surface. Section IV is devoted to the bulk dielectric tensor and electromagnetic modes of an infinite crystal, and Sec. V is concerned with the perturbative calculation of the optical properties of a crystalline surface. We present our conclusions in Sec. VI.

II. DISORDERED SYSTEM OF POLARIZABLE MOLECULES

We consider a disordered system of N ($\to\infty$) polarizable molecules, such as a liquid, with an isotropic polarizability $\alpha(\omega)$. In this case the spatial fluctuations come from the molecular structure of the system and from the microscopic density inhomogeneities. We also assume that the system is, on the average, isotropic and translationally invariant in space and time. In this case the macroscopic dielectric response $\hat{\epsilon}_M$ can be Fourier transformed as

$$\begin{aligned}\overleftrightarrow{\epsilon}_M(\mathbf{q},\omega) = \int dt' \int d^3r' \, \overleftrightarrow{\epsilon}_M(\mathbf{r}-\mathbf{r}';t-t') \\ \times e^{-i[\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')-\omega(t-t')]} ,\end{aligned} \tag{10}$$

where $\mathbf{q}$ is the wave vector and ω is the frequency.

In the calculation of the optical properties of the system it will be sufficient to consider the $\mathbf{q}\to 0$ limit of the response. In this limit, since there is no preferred direction of $\mathbf{q}$ (assuming continuity at $\mathbf{q}=\mathbf{0}$) the tensor $\overleftrightarrow{\epsilon}_M(\mathbf{q},\omega)$ becomes diagonal and it can be obtained from its longitudinal-longitudinal component; that is,

$$\epsilon_M^{ij}(\mathbf{q}) = \epsilon_M(\mathbf{q})\delta^{ij} = \hat{\mathbf{q}}\cdot\overleftrightarrow{\epsilon}_M^{\mathrm{LL}}(\mathbf{q})\cdot\hat{\mathbf{q}}\delta^{ij}, \quad q\to 0 \tag{11}$$

where $\hat{\mathbf{q}} = \mathbf{q}/q$ and the longitudinal projector $\overleftrightarrow{P}^{\mathrm{L}}(\mathbf{q}) = \hat{\mathbf{q}}\hat{\mathbf{q}}$ is taken in the $\mathbf{q}$ space representation. Here and in the following we will omit the explicit dependence on $\mathbf{q}$ and/or ω unless its omission will lead to confusion.

In order to relate $\overleftrightarrow{\epsilon}_M(\mathbf{q},\omega)$ to the molecular polarizability $\alpha(\omega)$ with the formalism developed above we will use the ensemble average $\hat{P}_a$. We will use

$$\langle F\rangle(\mathbf{r}) \equiv \sum_c P_c F_c(\mathbf{r}) \tag{12}$$

to denote the ensemble average in the $\mathbf{r}$ representation of a function F defined in the ensemble, and

$$\langle F\rangle(\mathbf{q})=\int d^3r\langle F\rangle(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}} \tag{13}$$

to denote its Fourier transform in $\mathbf{q}$ space, where P_c is the probability of finding the system in configuration c. Since $\langle F\rangle$ is configuration independent,

$$\hat{P}_a\hat{O}\hat{P}_aF=\langle\hat{O}\rangle\langle F\rangle \tag{14}$$

for any operator $\hat{O}$, and Eq. (3) can be written as

$$(\overleftrightarrow{\hat{\epsilon}}_M^{\mathrm{LL}})^{-1}(\mathbf{q})=\langle(\overleftrightarrow{\hat{\epsilon}}^{\mathrm{LL}})^{-1}\rangle(\mathbf{q})=\hat{\mathbf{q}}\langle(\epsilon^{\mathrm{cc}})^{-1}\rangle(\mathbf{q})\hat{\mathbf{q}}\ , \tag{15}$$

which combined with Eq. (11) gives

$$\frac{1}{\epsilon_M}=\langle(\epsilon^{\mathrm{cc}})^{-1}\rangle(\mathbf{q}),\quad \mathbf{q}\to\mathbf{0}\ . \tag{16}$$

Thus the problem reduces to the calculation of the ensemble average of $(\hat{\epsilon}^{\mathrm{cc}})^{-1}$ in terms of the molecular polarizability α.

Since $(\hat{\epsilon}^{\mathrm{cc}})^{-1}$ is the total-charge response of the system to an external charge [Eq. (6)], one can start its calculation by considering that in a configuration in which the molecules are located at $\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_N$, the induced dipole moment of the lth molecule in the presence of an external field $\mathbf{E}^{\mathrm{ext}}(\mathbf{r})$, ignoring retardation effects, is given by

$$p_1=\alpha\left[\mathbf{E}_l^{\mathrm{ext}}+\sum_{m\ (\neq l)}\overleftrightarrow{\mathrm{T}}_{lm}\mathbf{p}_m\right],\quad 1=1,2,\ldots,N \tag{17}$$

where

$$\overleftrightarrow{\mathrm{T}}_{lm}=\nabla_l\nabla_l\frac{1}{|\mathbf{R}_l-\mathbf{R}_m|}\equiv\overleftrightarrow{\mathrm{T}}(\mathbf{R}_l-\mathbf{R}_m) \tag{18}$$

is the dipolar tensor, ∇_l denotes derivatives with respect to $\mathbf{R}_l$, and $\mathbf{E}_l^{\mathrm{ext}}\equiv\mathbf{E}^{\mathrm{ext}}(\mathbf{R}_l)$.

Defining a tensor matrix

$$\overleftrightarrow{\mathrm{U}}_{lm}=\overleftrightarrow{1}\delta_{lm}-\alpha\overleftrightarrow{\mathrm{T}}_{lm}(1-\delta_{lm})\ , \tag{19}$$

where $\overleftrightarrow{1}$ is the unit tensor, we can rewrite Eq. (17) as

$$\mathbf{p}_l=\alpha\sum_m(\overleftrightarrow{\mathrm{U}}^{-1})_{lm}\mathbf{E}_m^{\mathrm{ext}}\ , \tag{20}$$

where in order to obtain $(\overleftrightarrow{\mathrm{U}}^{-1})_{lm}$, one first inverts the matrix and afterwards takes the lm element.

If the external field is generated by an external unit point charge located at $\mathbf{r}'$, the total charge density is given by

$$\rho(\mathbf{r})=\delta(\mathbf{r}-\mathbf{r}')-\sum_l\nabla\delta(\mathbf{r}-\mathbf{R}_l)\cdot\mathbf{p}_l\ ,$$

which together with Eq. (20) yields

$$\rho(\mathbf{r})=\delta(\mathbf{r}-\mathbf{r}')-\alpha\sum_{l,m}\nabla\delta(\mathbf{r}-\mathbf{R}_l)\cdot(\overleftrightarrow{\mathrm{U}}^{-1})_{lm}\cdot\frac{\mathbf{R}_m-\mathbf{r}'}{|\mathbf{R}_m-\mathbf{r}'|^3}\ .$$

Therefore, using Eq. (6) we can immediately write

$$(\epsilon^{\mathrm{cc}})^{-1}(\mathbf{r},\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}')-\alpha\sum_{l,m}\nabla\delta(\mathbf{r}-\mathbf{R}_l)\cdot(\overleftrightarrow{\mathrm{U}}^{-1})_{lm}\cdot\frac{\mathbf{R}_m-\mathbf{r}'}{|\mathbf{R}_m-\mathbf{r}'|^3}\ , \tag{21}$$

and Eq. (16) becomes

$$\frac{1}{\epsilon_M(\mathbf{q})}=1-\alpha\left\langle\sum_{l,m}e^{-i\mathbf{q}\cdot\mathbf{R}_l}i\mathbf{q}\cdot(\overleftrightarrow{\mathrm{U}}^{-1})_{lm}\cdot\frac{\mathbf{R}_m}{R_m^3}\right\rangle,\quad \mathbf{q}\to\mathbf{0}\ . \tag{22}$$

Although the starting point of other formulations of the local-field effect in this system is the same as in Eq. (17), Eq. (22) is the result of a straightforward procedure based on the general formalism developed above.

Although Eq. (22) is appropriate for any value of α, we proceed with the calculation by making a series expansion of $(\overleftrightarrow{\mathrm{U}}^{-1})_{lm}$ in powers of α,[51]

$$(\overleftrightarrow{\mathrm{U}}^{-1})_{lm}=\overleftrightarrow{1}\delta_{lm}+\alpha\overleftrightarrow{\mathrm{T}}_{lm}(1-\delta_{lm})+\alpha^2\sum_{n\ (\neq l,m)}\overleftrightarrow{\mathrm{T}}_{ln}\cdot\overleftrightarrow{\mathrm{T}}_{nm}+\alpha^3\sum_{\substack{n\ (\neq 1),\\ p\ (\neq n,m)}}\overleftrightarrow{\mathrm{T}}_{ln}\cdot\overleftrightarrow{\mathrm{T}}_{np}\cdot\overleftrightarrow{\mathrm{T}}_{pm}+\cdots\ , \tag{23}$$

which leads to a power expansion for $1/\epsilon_M$ as

$$\frac{1}{\epsilon_M(\mathbf{q})}=1-\sum_{t=1}^{\infty}\alpha^t\chi^{(t)}(\mathbf{q})\ , \tag{24}$$

where $\chi^{(t)}$ is the coefficient of α^t in Eq. (22).

The first term of the series is simply

$$\chi^{(1)}=4\pi n\ , \tag{25}$$

where n is the average density.

Since the second term depends only on the coordinates of two particles we can write

$$\chi^{(2)}=\left\langle\sum_{l\ (\neq m)}e^{-i\mathbf{q}\cdot\mathbf{R}_l}i\mathbf{q}\cdot\overleftrightarrow{\mathrm{T}}_{lm}\cdot\frac{\mathbf{R}_m}{R_m^3}\right\rangle$$
$$=\int d^3X_1\int d^3X_2\,e^{-i\mathbf{q}\cdot\mathbf{X}_1}i\mathbf{q}\cdot\overleftrightarrow{\mathrm{T}}(\mathbf{X}_1-\mathbf{X}_2)\cdot\frac{\mathbf{X}_2}{X_2^3}\rho^{(2)}(\mathbf{X}_1,\mathbf{X}_2)\ , \tag{26}$$

where $\rho^{(2)}(\mathbf{X}_1,\mathbf{X}_2)d^3X_1\,d^3X_2$ is the probability of finding a molecule at d^3X_1 and another molecule at d^3X_2. Defining the two-particle correlation function $g^{(2)}(|\mathbf{X}_1-\mathbf{X}_2|)$ through

$$\rho^{(2)}(\mathbf{X}_1,\mathbf{X}_2)=n^2g^{(2)}(|\mathbf{X}_1-\mathbf{X}_2|)\ , \tag{27}$$

we obtain

$$\chi^{(2)}(\mathbf{q})=4\pi n^2\int d^3X\, e^{i\mathbf{q}\cdot\mathbf{X}}g^{(2)}(X)\hat{\mathbf{q}}\cdot\nabla\hat{\mathbf{q}}\cdot\nabla\frac{1}{X}\,, \tag{28}$$

where the translational invariance of the system has been used. If $g^{(2)}(0)=0$ and $g^{(2)}(X)$ goes to 1 at distances greater than the correlation length d, the integral in Eq. (68) is readily evaluated in the limit $qd\ll 1$,[52] and one obtains

$$\chi^{(2)}=-4\pi n^2\frac{8\pi}{3}\,. \tag{29}$$

The remaining terms can be similarly written as

$$\chi^{(m)}(\mathbf{q})=\int d^3X_1\int d^3X_2\cdots\int d^3X_m\, e^{-i\mathbf{q}\cdot\mathbf{X}_1}i\mathbf{q}\cdot\overleftrightarrow{\mathbf{T}}(\mathbf{X}_1-\mathbf{X}_2)\cdot\overleftrightarrow{\mathbf{T}}(\mathbf{X}_2-\mathbf{X}_3)\cdot\cdots\cdot\overleftrightarrow{\mathbf{T}}(\mathbf{X}_{m-1}-\mathbf{X}_m)\cdot\frac{\mathbf{X}_m}{X_m^3}$$

$$\times\rho^{(m)}(\mathbf{X}_1,X_2,\ldots,\mathbf{X}_m),\quad m=3,4,\ldots,N \tag{30}$$

where $\rho^{(m)}(\mathbf{X}_1,\mathbf{X}_2,\ldots,\mathbf{X}_m)d^3X_1\,d^3X_2\cdots d^3X_m$ is the probability of finding one molecule in the volume element d^3X_1, another in d^3X_2, some molecule in d^3X_3 which is not the same as the one in d^3X_2 but might be the one in d^3X_1, etc.

To evaluate the integrals in (30) we write

$$\rho^{(m)}\equiv\rho_0^{(m)}+\Delta\rho^{(m)}\,, \tag{31}$$

and correspondingly

$$\chi^{(m)}=\chi_0^{(m)}+\Delta\chi^{(m)}\,, \tag{32}$$

where

$$\rho_0^{(m)}(\mathbf{X}_1,\mathbf{X}_2,\ldots,\mathbf{X}_m)\equiv n^m g^{(2)}(\mathbf{X}_1-\mathbf{X}_2)g^{(2)}(\mathbf{X}_2-\mathbf{X}_3)\times\cdots\times g^{(2)}(\mathbf{X}_{m-1}-\mathbf{X}_m) \tag{33}$$

is obtained by neglecting the correlations between the molecule at $\mathbf{X}_l$ and the molecules at $\mathbf{X}_{l+2},\mathbf{X}_{l+3},\ldots,\mathbf{X}_m$ for $l=1,2,\ldots,m-2$.

To calculate $\chi_0^{(m)}$ we have to perform the same integral as in Eq. (28) and we obtain immediately

$$\chi_0^{(m)}=4\pi n^m(-\tfrac{8}{3}\pi)^m\,, \tag{34}$$

and, from Eq. (34)

$$\frac{1}{\epsilon_M}=\frac{1}{\epsilon_{\rm CM}}=\sum_{t=3}^{\infty}\alpha^t\Delta\chi^{(t)}\,, \tag{35}$$

where

$$\frac{1}{\epsilon_{\rm CM}}\equiv\frac{4\pi n\alpha}{1+\frac{8}{3}\pi n\alpha} \tag{36}$$

is the inverse of the well-known Clausius-Mossotti dielectric function.

To calculate the corrections to the Clausius-Mossotti result we need expressions for $\Delta\rho^{(m)}$. For example, we can write

$$\rho^{(3)}(\mathbf{X}_1,\mathbf{X}_2,\mathbf{X}_3)=n^2g^{(2)}(\,|\mathbf{X}_1-\mathbf{X}_2|\,)\delta(\mathbf{X}_3-\mathbf{X}_1)$$
$$+n^3g^{(3)}(\mathbf{X}_1-\mathbf{X}_2,\mathbf{X}_2-\mathbf{X}_3)\,, \tag{37}$$

where $g^{(3)}$ is the three-particle correlation function. The first term on the right-hand side of Eq. (37) is the probability density of finding one molecule at $\mathbf{X}_2$ and a second molecule at both $\mathbf{X}_1$ and $\mathbf{X}_3$. The second term is the probability density of finding three different particles at $\mathbf{X}_1,\mathbf{X}_2,\mathbf{X}_3$. From Eq. (37) we get the first correction term:

$$\Delta\chi^{(3)}=\frac{4\pi n}{\alpha^2}S^{(2)}\,, \tag{38}$$

where

$$S^{(2)}=\alpha^2\left[8\pi n\int_0^{\infty}dX\frac{g^{(2)}(X)}{X^4}+2n^2\int d^3X_1\int d^3X_2\frac{P_2(\cos\theta)}{X_1^3X_2^3}[g^{(3)}(\mathbf{X}_1,\mathbf{X}_2)-g^{(2)}(X_1)g^{(2)}(X_2)]\right]. \tag{39}$$

Here θ is the angle between $\mathbf{X}_1$ and $\mathbf{X}_2$, and P_2 is the Legendre polynomial of second degree. Finally we write Eq. (35) as

$$\frac{\epsilon_M-1}{\epsilon_M+2}=\frac{4\pi}{3}n\alpha[1+S^{(2)}+O(\alpha^3)]\,, \tag{40}$$

which is the familiar Kirkwood-Yvon result.[53]

We want to point out that more accurate calculations[28–33] of the macroscopic response of polarizable liquids can also be performed starting from Eqs. (16) or (22), as long as the fluctuation length-scale is much smaller than the free-space wavelength. However, the purpose of the calculation above is to illustrate how our general formalism, contained in Eqs. (1)–(9), can be applied straightforwardly to a system of point-polarizable atoms in order to obtain nontrivial results. More elaborate calculations will be the object of further research.

III. SURFACE ROUGHNESS

In this section we apply the formalism developed above and the perturbative formulas of Ref. 54 to calculate the ellipsometric coefficients, the reflectance and the surface-plasmon-polariton dispersion relation of a semi-infinite medium bounded by a microscopically rough surface. By microscopically rough we mean that the roughness length scale l along the surface is much smaller than the free-space wavelength λ. This implies that the scattered fields are unable to leave the surface. For this reason, the optical properties of this surfaces are becoming important for experimental surface studies.[55]

The model we use is described by the local isotropic dielectric response

$$\begin{aligned}\overleftrightarrow{\epsilon}(\mathbf{r},\mathbf{r}')&=\epsilon(\mathbf{r})\hat{1}\delta(\mathbf{r}-\mathbf{r}')\\&=[\epsilon_0\Theta(z-\xi(\boldsymbol{\rho}))+\Theta(\xi(\boldsymbol{\rho})-z)]\overleftrightarrow{1}\delta(\mathbf{r}-\mathbf{r}')\ ,\end{aligned}\tag{41}$$

where Θ is the unit step function, $\boldsymbol{\rho}=(x,y,0)$, and $\xi(\boldsymbol{\rho})$ is the height of the actual surface of the medium above a nominal plane surface at $z=0$, chosen such that $\langle\xi(\boldsymbol{\rho})\rangle=0$. We will assume that the system has, on the average, translational invariance along the x-y plane.

We note that although the response (41) is already a macroscopic response (since it does not present the fluctuations due to the atomic structure of the medium), it might also be considered a microscopic response since it has microscopic spatial fluctuations due to the rough surface profile. It is our purpose to average out this fluctuations with the methods developed in Ref. 1, using an ensemble average $\hat{P}_a$.

We expect that the macroscopic dielectric response of the system differs from the local response of a plane-bounded system

$$\begin{aligned}\boldsymbol{\epsilon}_p(\mathbf{r},\mathbf{r}')&=\epsilon_p(z)\overleftrightarrow{1}\delta(\mathbf{r}-\mathbf{r}')\\&\equiv[\epsilon_0\Theta(z)+\Theta(-z)]\overleftrightarrow{1}\delta(\mathbf{r}-\mathbf{r}')\end{aligned}\tag{42}$$

only in a small region around the $z=0$ plane. Then, the optical properties of the system can be calculated using a perturbative approach where the perturbations $\Delta\hat{\epsilon}_M$ and $\Delta\hat{\epsilon}_M^{-1}$ are defined by

$$\begin{aligned}\Delta\hat{\epsilon}_M&=\hat{\epsilon}_M-\hat{\epsilon}_p\ ,\\\Delta\hat{\epsilon}_M^{-1}&=\hat{\epsilon}_M^{-1}-\hat{\epsilon}_p^{-1}\ ,\end{aligned}\tag{43}$$

and $\hat{\epsilon}_p$ plays the role of the unperturbed substrate.

The surface impedances Z_p and Z_s for p and s polarization are taken from Eqs. (32) and (33) of Ref. 54, which can be written to lowest order in $\Delta\overleftrightarrow{\epsilon}_M$ as

$$Z_p=\frac{kc-iQkc((\Delta\epsilon_M^{xz}(\epsilon_0^{zz})^{-1}))+i\epsilon_0Q^2c((\Delta(\epsilon_M^{zz})^{-1}))}{\epsilon_0\omega-i\omega k((\Delta\epsilon_M^{xx}))-i\epsilon_0\omega Q(((\epsilon_p^{zz})^{-1}\Delta\epsilon_M^{zx}))}\tag{44}$$

and

$$Z_s=\frac{\omega c}{kc^2-i\omega^2((\Delta\epsilon_M^{yy}))}\ .\tag{45}$$

Here ω is the frequency of the incident light, $\mathbf{Q}=(Q,0,0)$ the component of its wave vector parallel to the surface, $k=(\epsilon_0\omega^2/c^2-Q^2)^{1/2}$ [with $\mathrm{Im}(k)>0$ or else $\mathrm{Im}(k)=0$ and $\mathrm{Re}(k)\geq 0$] is the component normal to the surface of the wave vector inside the substrate and we introduced the notation

$$\begin{aligned}((O))\equiv\int dz\int dz'\int d^2(\rho-\rho')e^{-i\mathbf{Q}\cdot(\boldsymbol{\rho}-\boldsymbol{\rho}')}\\\times O(\boldsymbol{\rho}-\boldsymbol{\rho}',z,z')\end{aligned}\tag{46}$$

for any operator $\hat{O}$ with translational invariance along the surface. We have also assumed that the ensemble is symmetric under a $y\rightarrow -y$ reflection so there is no s-p mixing.

If we now define $\Delta\hat{\epsilon}$ and $\Delta\hat{\epsilon}^{-1}$ as the perturbations of the microscopic dielectric response relative to the same reference substrate given in Eq. (42), that is

$$\begin{aligned}\Delta\hat{\epsilon}&=\hat{\epsilon}-\hat{\epsilon}_p\ ,\\\Delta\hat{\epsilon}^{-1}&=\hat{\epsilon}^{-1}-\hat{\epsilon}_p^{-1}\ ,\end{aligned}\tag{47}$$

we can use Eqs. (1) and (2) to relate $\Delta\hat{\epsilon}_M$ and $\Delta\hat{\epsilon}_M^{-1}$ to $\Delta\hat{\epsilon}$ and $\Delta\hat{\epsilon}^{-1}$. Doing this, and using the property of the ensemble average expressed in Eq. (14), we obtain to lowest order in the microscopic fluctuations

$$\Delta\hat{\epsilon}_M=\langle\Delta\hat{\epsilon}\rangle-\langle\Delta\hat{\epsilon}(\hat{\epsilon}_p^{\mathrm{LL}})^{-1}\Delta\hat{\epsilon}\rangle+\langle\Delta\hat{\epsilon}\rangle(\hat{\epsilon}_p^{\mathrm{LL}})^{-1}\langle\Delta\hat{\epsilon}\rangle\ ,\tag{48}$$

$$\begin{aligned}\Delta\hat{\epsilon}_M^{-1}=\langle\Delta\hat{\epsilon}^{-1}\rangle-\langle\Delta\hat{\epsilon}^{-1}[(\hat{\epsilon}_p^{-1})^{\mathrm{TT}}]^{-1}\Delta\hat{\epsilon}^{-1}\rangle\\+\langle\Delta\hat{\epsilon}^{-1}\rangle[(\hat{\epsilon}_p^{-1})^{\mathrm{TT}}]^{-1}\langle\Delta\hat{\epsilon}^{-1}\rangle\ .\end{aligned}\tag{49}$$

We remark that $\Delta\hat{\epsilon}$ and $\Delta\hat{\epsilon}^{-1}$ are local isotropic operators which are different from zero in a region of the order of ξ around the xy plane, and we recall that $\langle\ \rangle$ denotes semble average.

First of all we have to calculate the longitudinal-longitudinal response of a flat bounded system. This is most readily done by relying on the interpretation discussed in Eq. (8): $[(\epsilon_p^{\mathrm{LL}})^{-1}]^{ij}(\mathbf{r},\mathbf{r}')$ describes the ith component of the longitudinal electric field at $\mathbf{r}$ produced by a point dipole $\mathbf{p}=-\hat{e}_j/(4\pi)$ at $\mathbf{r}'$ in the presence of a flat bounded system in the absence of retardation ($\hat{e}_j$ denotes a unit vector in the j direction). This field is easily calculated using image-charge theory, and we obtain

$$[(\epsilon_p^{\mathrm{LL}})^{-1}]^{ij}(\mathbf{r},\mathbf{r}')=-\frac{1}{4\pi}\partial_i\partial_j\times\begin{cases}\dfrac{1}{|\mathbf{r}-\mathbf{r}'|}+\beta_j\dfrac{1-\epsilon_0}{1+\epsilon_0}\dfrac{1}{|\mathbf{r}-\mathbf{r}''|} & \text{if } z<0,\ z'<0\\ \dfrac{2}{1+\epsilon_0}\dfrac{1}{|\mathbf{r}-\mathbf{r}'|} & \text{if } zz'<0\\ \dfrac{1}{\epsilon_0}\left[\dfrac{1}{|\mathbf{r}-\mathbf{r}'|}-\beta_j\dfrac{1-\epsilon_0}{1+\epsilon_0}\dfrac{1}{|\mathbf{r}-\mathbf{r}''|}\right] & \text{if } z>0,\ z'>0\ ,\end{cases} \tag{50}$$

where $i,j=x$ or z, $\beta_x=1$ and $\beta_z=-1$, and $\mathbf{r}''=(\boldsymbol{\rho}',-z')$. Now we use Eq. (9) to obtain

$$\{[(\epsilon_p^{-1})^{\mathrm{TT}}]^{-1}\}^{ij}(\mathbf{r},\mathbf{r}')=\epsilon_p(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')-\frac{1}{4\pi}\partial_i\partial_j\times\begin{cases}\dfrac{1}{|\mathbf{r}-\mathbf{r}'|}+\beta_j\dfrac{1-\epsilon_0}{1+\epsilon_0}\dfrac{1}{|\mathbf{r}-\mathbf{r}''|} & \text{if } z<0,\ z'<0\\ \dfrac{2\epsilon_0}{1+\epsilon_0}\dfrac{1}{|\mathbf{r}-\mathbf{r}'|} & \text{if } zz'<0\\ \epsilon_0\left[\dfrac{1}{|\mathbf{r}-\mathbf{r}'|}-\beta_j\dfrac{1-\epsilon_0}{1+\epsilon_0}\dfrac{1}{|\mathbf{r}-\mathbf{r}''|}\right] & \text{if } z>0,\ z'>0\ .\end{cases} \tag{51}$$

To proceed, we recall that the component parallel to the surface of the electric field and the component normal to the surface of the displacement field are continuous across the boundary, and they have a length scale of variation along the z direction as big as the length scale of variation along the surface. Thus, if the surface-roughness scale of variation d is much bigger than the surface height ξ (remember also the condition $d\ll\lambda$), it is reasonable to make a first-order Taylor-series expansion of $\Delta\epsilon^{xx}$, $\Delta\epsilon^{yy}$, and $\Delta(\epsilon^{-1})^{zz}$:

$$\Delta\epsilon^{xx}(\mathbf{r})=\Delta\epsilon^{yy}(\mathbf{r})\approx(1-\epsilon_0)\xi(\boldsymbol{\rho})\delta(z)\ , \tag{52}$$

$$\Delta(\epsilon^{-1})^{zz}(\mathbf{r})\approx-\frac{1-\epsilon_0}{\epsilon_0}\xi(\boldsymbol{\rho})\delta(z)\ . \tag{53}$$

Notice that since $E^z(\mathbf{r})$ has abrupt variations near $z\approx0$, it makes not sense to do a Taylor-series expansion of $\Delta\epsilon^{zz}$. However, using Eq. (53), we can write

$$\begin{aligned}\Delta\epsilon^{zz}(\mathbf{r})&\approx-\epsilon_p^2(z)\Delta(\epsilon^{-1})^{zz}(\mathbf{r})\\&=\epsilon_p^2(z)\frac{1-\epsilon_0}{\epsilon_0}\xi(\boldsymbol{\rho})\delta(z)\ ,\end{aligned} \tag{54}$$

and, although this expression is ambiguous in $z=0$, it gives well-defined expressions in the final results.

Substituting Eqs. (50)–(54) into Eqs. (48) and (49), one gets expressions for $\Delta\epsilon_M(\mathbf{r},\mathbf{r}')$ and $\Delta(\epsilon_M^{-1})(\mathbf{r},\mathbf{r}')$ which can be used to calculate the following terms required in expressions (44) and (45):

$$((\Delta\epsilon_M^{xx}))=-\frac{(1-\epsilon_0)^2}{1+\epsilon_0}\langle\xi^2\rangle\int\frac{d^2Q'}{(2\pi)^2}g(\mathbf{Q}-\mathbf{Q}')\frac{(Q_x')^2}{Q'}\ , \tag{55}$$

$$((\Delta(\epsilon_M^{zz})^{-1}))=-\frac{(1-\epsilon_0)^2}{\epsilon_0(1+\epsilon_0)}\langle\xi^2\rangle\int\frac{d^2Q'}{(2\pi)^2}g(\mathbf{Q}-\mathbf{Q}')Q'\ , \tag{56}$$

$$(((\epsilon_p^{zz})^{-1}\Delta\epsilon_M^{zx}))=-\frac{(1-\epsilon_0)^2}{1+\epsilon_0}\langle\xi^2\rangle\int\frac{d^2Q'}{(2\pi)^2}g(\mathbf{Q}-\mathbf{Q}')iQ_x'\times\begin{cases}1\\-\dfrac{1}{\epsilon_0}\end{cases}, \tag{57}$$

$$((\Delta\epsilon_M^{xz}(\epsilon_p^{zz})^{-1}))=-\frac{(1-\epsilon_0)^2}{1+\epsilon_0}\langle\xi^2\rangle\int\frac{d^2Q'}{(2\pi)^2}g(\mathbf{Q}-\mathbf{Q}')iQ_x'\times\begin{cases}\dfrac{1}{\epsilon_0}\\-1\end{cases}, \tag{58}$$

where $g(\mathbf{Q})$ is the Fourier transform of the roughness autocorrelation function defined by

$$\langle\xi(\boldsymbol{\rho})\xi(\boldsymbol{\rho}')\rangle=\langle\xi^2\rangle g(\boldsymbol{\rho}-\boldsymbol{\rho}')\ . \tag{59}$$

The expression for $((\Delta\epsilon_M^{yy}))$ is similar to Eq. (55).

Notice that Eqs. (57) and (58) give two different results depending on how the $z,z'\to0$ limit of $(\overleftrightarrow{\epsilon}^{\mathrm{LL}})^{-1}(\mathbf{r},\mathbf{r}')$, required in Eqs. (48) and (49) by the presence in Eqs. (52)–(54) of the δ functions, is taken. The upper choice in Eqs. (57) and (58) is obtained when we take these limits in the order $z\to0$, $z'\to0^-$ or in the order $z'\to0$, $z\to0^+$, and the lower choice is obtained when we take the limits in the order $z\to0$, $z'\to0^+$ or in the order $z'\to0$, $z\to0^-$. This ambiguity appears in $(\overleftrightarrow{\epsilon}_p^{\mathrm{LL}})^{-1}(\mathbf{r},\mathbf{r}')$ according to its

interpretation given above as a consequence of the singularities in the charge density and in the electric field of a point dipole.

However, we point out that to the order of $\langle\xi^2\rangle$ the surface impedance obtained by substitution of Eqs. (55)–(58) in Eqs. (44) and (45) is not ambiguous. Therefore it is not necessary for us to specify the way in which the $z,z'\to 0$ limit is taken, as was previously believed.[46] The reason for this is that, as discussed above, in Eq. (53) we made a Taylor-series expansion of $(\epsilon^{-1})^{zz}(\mathbf{r})$ instead of making a Taylor-series expansion of $\epsilon^{zz}(\mathbf{r})$. We do not have to worry about the ambiguities in the higher-order terms since the calculation above is only valid to order $\langle\xi^2\rangle$.

Having the surface impedance of the system we can easily calculate its observable optical properties, such as its ellipsometric coefficients ψ and Δ, given by $tg\psi e^{i\Delta}=r_p/r_s$ in terms of the s and p reflection amplitudes r_s and r_p. These are in turn given by

$$r_s=\frac{Z_s-Z_s^V}{Z_s+Z_s^V}=r_s^0\left[1-2iq\frac{1-\epsilon_0}{1+\epsilon_0}\langle\xi^2\rangle\int\frac{d^2Q'}{(2\pi)^2}g(\mathbf{Q}-\mathbf{Q}')\frac{(Q_y')^2}{Q'}\right], \tag{60}$$

and

$$r_p=\frac{Z_p^V-Z_p}{Z_p^V+Z_p}=r_p^0\left[1+\frac{2iq}{Q^2-\epsilon_0 q^2}\frac{1-\epsilon_0}{1+\epsilon_0}\langle\xi^2\rangle\int\frac{d^2Q'}{(2\pi)^2}\frac{g(\mathbf{Q}-\mathbf{Q}')}{Q'}[k^2(Q_x')^2+\epsilon_0Q^2(Q')^2+(\epsilon_0-1)QkQ'Q_x']\right]. \tag{61}$$

Here we introduced the surface impedance of vacuum $Z_s^V=\omega/(qc)$ and $Z_p^V=qc/\omega$, where q is the normal to the surface component of the wave vector in vacuum,

$$q^2=\frac{\omega^2}{c^2}-Q^2,\quad \mathrm{Im}(q)>0 \text{ or else}$$
$$\mathrm{Im}(q)=0 \text{ and } \mathrm{Re}\,(q)\geq 0\,, \tag{62}$$

and the Fresnel reflection amplitudes $r_s^0=(q-k)/(q+k)$ and $r_p^0=(\epsilon_0 q-k)/(\epsilon_0 q+k)$.

We can also calculate the relative change in reflectance between the rough and the plane bounded system, $\Delta R/R\equiv(|r|^2-|r^0|^2)/|r^0|^2$, and we obtain

$$\frac{\Delta R_s}{R_s}=4\langle\xi^2\rangle\mathrm{Im}\left[q\frac{1-\epsilon_0}{1+\epsilon_0}\int\frac{d^2Q'}{(2\pi)^2}g(\mathbf{Q}-\mathbf{Q}')\frac{(Q_y')^2}{Q'}\right], \tag{63}$$

and

$$\frac{\Delta R_p}{R_p}=-4\langle\xi^2\rangle\mathrm{Im}\left[\frac{q}{Q^2-\epsilon_0q^2}\frac{1-\epsilon_0}{1+\epsilon_0}\int\frac{d^2Q'}{(2\pi)^2}\frac{g(\mathbf{Q}-\mathbf{Q}')}{Q'}[k^2(Q_x')^2+\epsilon_0Q^2(Q')^2+(\epsilon_0-1)QkQ'Q_x']\right]. \tag{64}$$

Finally, the surface-plasmon–polariton dispersion relation is given by $Z_p^V+Z_p=0$ and becomes

$$\epsilon_0 q+k-i\frac{(1-\epsilon_0)^2}{1+\epsilon_0}\langle\xi^2\rangle\int\frac{d^2Q'}{(2\pi)^2}\frac{g(\mathbf{Q}-\mathbf{Q}')}{Q'}(\mathbf{Q}\cdot\mathbf{Q}'+iQ'q)(\mathbf{Q}\cdot\mathbf{Q}'+iQ'k)=0\,, \tag{65}$$

using that, to order 0 in $\langle\xi^2\rangle$, $Q^2=-qk$ and $\epsilon_0 q+k=0$.

Since we assumed that the surface-profile scale of variation is much smaller than the free-space wavelength, our results are correct when the autocorrelation function is such that $g(\mathbf{Q})=0$ unless $Q\gg\omega/c$. It can easily be shown that under this condition our results are the same as those of Refs. 56 and 57.

Although the model [Eq. (41)] that we used for the rough surface is quite conventional, the procedure by which we arrived at our results is not. First we obtained the perturbation in the macroscopic dielectric response, produced near the surface by the rough profile, using our general local-field-effect theory, and then we obtained the optical properties of the system using standard formulas. By using the appropriate microscopic response fluctuations, the adequate image charge theory,[58] and the same procedures, we could calculate the optical properties of rough nonlocal metallic surfaces. These show interesting effects such as the coupling between the roughness-induced small-wavelength surface plasmons with the bulk elementary excitations such as plasma waves.[50] This topic is presently under investigation.

IV. INFINITE CRYSTAL

In this section we obtain expressions for the macroscopic dielectric response and bulk normal modes of a perfect crystal without adopting any model for its microscopic response, but exploiting its ideal periodicity. Thus the consequences of deformations such as the elasto-optic effect[59] are beyond this section's scope.

We consider a system which remains invariant under translation by any vector $\mathbf{R}$ of a three-dimensional periodic lattice. This invariance manifests itself in the microscopic nonlocal dielectric function $\overleftrightarrow{\epsilon}(\mathbf{r},\mathbf{r}')$ as

$$\overleftrightarrow{\epsilon}(\mathbf{r}+\mathbf{R},\mathbf{r}'+\mathbf{R})=\overleftrightarrow{\epsilon}(\mathbf{r},\mathbf{r}') . \tag{66}$$

To take advantage of this symmetry, we find it convenient to express the fields as a superposition of Bloch waves through

$$\begin{aligned}\mathbf{E}(\mathbf{r})&=\frac{\Omega}{(2\pi)^3}\int_0 d^3q\,\mathbf{E}(\mathbf{q},\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}\\&=\frac{\Omega}{(2\pi)^3}\int_0 d^3q\sum_{\mathbf{K}}\mathbf{E}_{\mathbf{K}}(q)e^{i(\mathbf{q}+\mathbf{K})\cdot\mathbf{r}} ,\end{aligned} \tag{67}$$

and similar equations for the other fields of interest, where Ω is the volume of the unit cell, the integrals $\int_0 d^3q$ are over the first Brillouin zone, and $\mathbf{E}(\mathbf{q},\mathbf{r})$ is a periodic function of both the position $\mathbf{r}$ and the pseudomomentum $\mathbf{q}$, which yields a Bloch function when multiplied by the phase factor $e^{i\mathbf{q}\cdot\mathbf{r}}$. The Fourier series coefficients of $\mathbf{E}(\mathbf{q},\mathbf{r})$ are given by $\mathbf{E}_{\mathbf{K}}(\mathbf{q})$, which is related to the usual Fourier transform of $\mathbf{E}(\mathbf{r})$ by $\mathbf{E}_{\mathbf{K}}(\mathbf{q})=(1/\Omega)\mathbf{E}(\mathbf{q}+\mathbf{K})$, where the wave vectors $\mathbf{K}$ form the reciprocal lattice defined by $e^{i\mathbf{K}\cdot\mathbf{R}}\equiv 1$.

Then we can write $\mathbf{D}=\hat{\epsilon}\mathbf{E}$ as

$$\mathbf{D}_{\mathbf{K}}(\mathbf{q})=\sum_{\mathbf{K}'}\overleftrightarrow{\epsilon}_{\mathbf{K}\mathbf{K}'}(\mathbf{q})\mathbf{E}_{\mathbf{K}'}(\mathbf{q}) , \tag{68}$$

where we defined the dielectric matrix

$$\overleftrightarrow{\epsilon}_{\mathbf{K}\mathbf{K}'}(\mathbf{q})=\frac{1}{\Omega}\int_0 d^3r\int_0 d^3r'\sum_{\mathbf{R}}\overleftrightarrow{\epsilon}(\mathbf{r}+\mathbf{R},\mathbf{r}')\times e^{-i[(\mathbf{q}+\mathbf{K})\cdot(\mathbf{r}+\mathbf{R})-(\mathbf{q}+\mathbf{K}')\cdot\mathbf{r}']} \tag{69}$$

and the integrals $\int_0 d^3r$ are over the unit cell. Equation (68) expresses the conservation of the pseudomomentum $\mathbf{q}$, although the momentum $\mathbf{q}+\mathbf{K}$ is not conserved.

The longitudinal projector $\hat{P}^L$ is given in this representation by the matrix

$$\overleftrightarrow{P}^{\mathrm{L}}_{\mathbf{K}\mathbf{K}'}(\mathbf{q})=\frac{\mathbf{q}+\mathbf{K}}{|\mathbf{q}+\mathbf{K}|}\frac{\mathbf{q}+\mathbf{K}}{|\mathbf{q}+\mathbf{K}|}\delta_{\mathbf{K}\mathbf{K}'} , \tag{70}$$

so that for any vector field $\mathbf{F}_{\mathbf{K}}(\mathbf{q})$,

$$\mathbf{F}^{\mathrm{L}}_{\mathbf{K}}(\mathbf{q})=\frac{\mathbf{q}+\mathbf{K}}{|\mathbf{q}+\mathbf{K}|}\frac{\mathbf{q}+\mathbf{K}}{|\mathbf{q}+\mathbf{K}|}\cdot\mathbf{F}_{\mathbf{K}}(\mathbf{q}) . \tag{71}$$

As an averaging procedure we choose a truncation that eliminates all wave vectors outside the first Brillouin zone. Then the average projector $\hat{P}_a$ is represented by the matrix

$$(P_a)_{\mathbf{K}\mathbf{K}'}(\mathbf{q})=\delta_{\mathbf{K}0}\delta_{\mathbf{K}'0} , \tag{72}$$

so that for any function $G_{\mathbf{K}}(\mathbf{q})$,

$$(G_a)_{\mathbf{K}}(\mathbf{q})\equiv G_0(\mathbf{q})\delta_{\mathbf{K}0} . \tag{73}$$

Then, Eqs. (1)—(4) immediately give

$$\overleftrightarrow{\epsilon}_M=\overleftrightarrow{\epsilon}_{00}-\sum_{\mathbf{K},\mathbf{K}'\,(\neq 0)}\overleftrightarrow{\epsilon}_{0\mathbf{K}}(\overleftrightarrow{\epsilon}^{\mathrm{LL}}_r)^{-1}_{\mathbf{K}\mathbf{K}'}\overleftrightarrow{\epsilon}_{\mathbf{K}'0} , \tag{74}$$

$$\epsilon^{-1}_M=\overleftrightarrow{\epsilon}^{-1}_{00}-\sum_{\mathbf{K},\mathbf{K}'\,(\neq 0)}\overleftrightarrow{\epsilon}^{-1}_{0\mathbf{K}}[(\overleftrightarrow{\epsilon}^{-1})^{\mathrm{TT}}_r]^{-1}_{\mathbf{K}\mathbf{K}'}\overleftrightarrow{\epsilon}^{-1}_{\mathbf{K}'0} , \tag{75}$$

$$\begin{aligned}(\overleftrightarrow{\epsilon}^{\mathrm{LL}}_M)^{-1}&=(\overleftrightarrow{\epsilon}^{\mathrm{LL}})^{-1}_{00}=(\epsilon^{\mathrm{cc}})^{-1}_{00}\hat{\mathbf{q}}\hat{\mathbf{q}}\\&=(\epsilon^{\phi\phi})^{-1}_{00}\hat{\mathbf{q}}\hat{\mathbf{q}} ,\end{aligned} \tag{76}$$

$$[(\overleftrightarrow{\epsilon}^{-1}_M)^{\mathrm{TT}}]^{-1}=[(\overleftrightarrow{\epsilon}^{-1})^{\mathrm{TT}}]^{-1}_{00} , \tag{77}$$

where we omitted the explicit dependence on $\mathbf{q}$ of all quantities, $\hat{\mathbf{q}}=\mathbf{q}/q$ and the subscript r in $(\overleftrightarrow{\epsilon}^{\mathrm{LL}}_r)^{-1}_{\mathbf{K}\mathbf{K}'}$ and $[(\overleftrightarrow{\epsilon}^{-1})^{\mathrm{TT}}_r]^{-1}_{\mathbf{K}\mathbf{K}'}$ is meant as a remainder to restrict the matrices $\overleftrightarrow{\epsilon}^{\mathrm{LL}}_{\mathbf{K}\mathbf{K}'}$ and $(\overleftrightarrow{\epsilon}^{-1})^{\mathrm{TT}}_{\mathbf{K}\mathbf{K}'}$ to reciprocal wave vectors $\mathbf{K},\mathbf{K}'\neq 0$ before attempting the matrix inversions. If we define now a scalar longitudinal response as

$$\epsilon^{\mathrm{LL}}_{\mathbf{K}\mathbf{K}'}(\mathbf{q})=\frac{\mathbf{q}+\mathbf{K}}{|\mathbf{q}+\mathbf{K}|}\cdot\overleftrightarrow{\epsilon}_{\mathbf{K}\mathbf{K}'}(\mathbf{q})\cdot\frac{\mathbf{q}+\mathbf{K}'}{|\mathbf{q}+\mathbf{K}'|} , \tag{78}$$

then we can also write

$$\frac{1}{\epsilon^{\mathrm{LL}}_M}=(\epsilon^{\mathrm{LL}})^{-1}_{00}=(\epsilon^{\mathrm{cc}})^{-1}_{00}=(\epsilon^{\phi\phi})^{-1}_{00} . \tag{79}$$

Equations (76) and (79) are well-known results first obtained by Adler[4] and Wiser[5] using the random-phase-approximation (RPA) expressions for the microscopic response, and neglecting longitudinal-transverse (LT) coupling. Here we found that these expressions are correct even in the presence of LT coupling, and that they do not depend on the microscopic theory used to obtain $\overleftrightarrow{\epsilon}_{\mathbf{K}\mathbf{K}'}(\mathbf{q})$.

Having expressions for the macroscopic response functions of a crystal we can easily obtain its optical properties following the usual procedures for homogeneous systems. As an illustration, we obtain below its electromagnetic normal modes taking into account its microscopic spatial fluctuations.[60] In the absence of external sources, Maxwell's equations give immediately

$$q^2\mathbf{E}^{\mathrm{T}}_a=\frac{\omega^2}{c^2}\mathbf{D}^{\mathrm{T}}_a , \tag{80}$$

which we write as

$$\left[q^2(\overleftrightarrow{\epsilon}^{-1}_M)^{\mathrm{TT}}-\frac{\omega^2}{c^2}\overleftrightarrow{1}\right]\cdot\mathbf{D}^{\mathrm{T}}_a=\mathbf{0} . \tag{81}$$

Using Eq. (77), we obtain the dispersion relation $\omega=\omega(\mathbf{q})$ of the normal modes of the system (those with $\mathbf{D}^{\mathrm{T}}_a\neq 0$), given implicitly by

$$\det\left[\left[\frac{qc}{\omega}\right]^2\overleftrightarrow{1}-[(\overleftrightarrow{\epsilon}_M^{-1})^{\mathrm{TT}}]^{-1}(\mathbf{q},\omega)\right]=\det\left[\left[\frac{qc}{\omega}\right]^2\overleftrightarrow{1}-[(\overleftrightarrow{\epsilon}^{-1})^{\mathrm{TT}}]_{00}^{-1}(\mathbf{q},\omega)\right]=0\ . \tag{82}$$

This relation was first obtained by Johnson.[13] We want to point out the difference between Johnson's and our own approach. In Ref. 13 Johnson obtained Eq. (82) by making an expansion in powers of $\mathbf{q}$ of the exact microscopic dispersion relation, and then he identified $(qc/\omega)^2$ as the macroscopic dielectric function. In our approach, we first obtained the macroscopic dielectric tensor from its definition as a response function, and afterwards we obtained the dispersion relation as a simple consequence of the macroscopic Maxwell's equations.

In the case of small macroscopic LT coupling, i.e., if $\overleftrightarrow{\epsilon}_M^{\mathrm{LT}}(\mathbf{q})$ and $\overleftrightarrow{\epsilon}_M^{\mathrm{TL}}(\mathbf{q})$ are small, we obtain, using Eq. (9) in Eq. (82), two kinds of modes: Modes of mostly transverse character with dispersion relation given approximately by

$$\det\left[\left[\frac{qc}{\omega}\right]^2\overleftrightarrow{1}-\overleftrightarrow{\epsilon}_M^{\mathrm{TT}}(\mathbf{q},\omega)\right]=0\ , \tag{83}$$

and modes of mostly longitudinal character given approximately by

$$\epsilon_M^{\mathrm{LL}}(\mathbf{q},\omega)=(\epsilon^{\mathrm{LL}})_{00}^{-1}(\mathbf{q},\omega)=0\ . \tag{84}$$

In the complete absence of LT coupling, Eq. (82) leads to pure transverse modes only, given exactly by Eq. (83). However, in this case there are also pure longitudinal modes obtained from Gauss's law, $\mathbf{D}_a^{\mathrm{L}}(\mathbf{q},\omega)=\epsilon_M^{\mathrm{LL}}(\mathbf{q},\omega)\mathbf{E}_a^{\mathrm{L}}(\mathbf{q},\omega)=0$, and given exactly by Eq. (84).

V. SEMI-INFINITE CRYSTAL

As our last example, we obtain several expressions for the macroscopic dielectric response near the surface of a crystal, and indicate how a perturbative theory can be used to calculate the influence of the surface on its optical properties. As in the preceding section, we focus our attention on the effects of periodicity, without referring to any specific microscopic model.

We consider a crystal whose translational symmetries along the z direction are removed by the presence of a bounding surface. However, if this surface is parallel to a family of crystalline planes, the crystal will have periodicity along the x-y plane. This periodicity manifests itself in the dielectric response as

$$\overleftrightarrow{\epsilon}(\mathbf{r}_{\parallel}+\mathbf{X},z,\mathbf{r}'_{\parallel}+\mathbf{X},z')=\overleftrightarrow{\epsilon}(\mathbf{r}_{\parallel},z,\mathbf{r}'_{\parallel},z')\ , \tag{85}$$

where $\mathbf{r}_{\parallel}$ is the projection of $\mathbf{r}$ onto the x-y plane and the vectors $\mathbf{X}$ form a two-dimensional (2D) periodic lattice.

As in the preceding section, to take advantage of this symmetry we express the fields as a superposition of 2D Bloch waves through

$$\begin{aligned}\mathbf{E}(\mathbf{r})&=\frac{A}{(2\pi)^2}\int_0 d^2Q\,\mathbf{E}(\mathbf{Q},\mathbf{r}_{\parallel},z)e^{i\mathbf{Q}\cdot\mathbf{r}_{\parallel}}\\&=\frac{A}{(2\pi)^2}\int_0 d^2Q\sum_{\mathbf{G}}\mathbf{E}_{\mathbf{G}}(\mathbf{Q},z)e^{i(\mathbf{Q}+\mathbf{G})\cdot\mathbf{r}_{\parallel}}\ ,\end{aligned} \tag{86}$$

where the integrals $\int_0 d^2Q$ are over the first 2D Brillouin zone, A is the area of the 2D unit cell, and $\mathbf{E}(\mathbf{Q},\mathbf{r}_{\parallel},z)$ is a periodic function of both 2D pseudomomentum $\mathbf{Q}$ and position $\mathbf{r}_{\parallel}$, which yields a 2D Bloch function when multiplied by the phase factor $e^{i\mathbf{Q}\cdot\mathbf{r}_{\parallel}}$. The Fourier series coefficients of $\mathbf{E}(\mathbf{Q},\mathbf{r}_{\parallel},z)$ are given by $\mathbf{E}_{\mathbf{G}}(\mathbf{Q},z)$, where the wave vectors $\mathbf{G}$ form the 2D reciprocal lattice defined by $e^{i\mathbf{G}\cdot\mathbf{X}}=1$. If the periodicity along the surface is independent of the distance to it, as in the case of a clean surface in the absence of reconstruction, then the 2D reciprocal lattice $\{\mathbf{G}\}$ is given simply by the x-y projections of the three-dimensional (3D) bulk reciprocal lattice $\{\mathbf{K}\}$. Otherwise there might be additional wave vectors $\mathbf{G}$.

Now we can write $\mathbf{D}=\hat{\epsilon}\mathbf{E}$ as

$$\mathbf{D}_{\mathbf{G}}(\mathbf{Q},z)=\sum_{\mathbf{G}'}\int_{-\infty}^{\infty}dz'\overleftrightarrow{\epsilon}_{\mathbf{G}\mathbf{G}'}(\mathbf{Q},z,z')\mathbf{E}_{\mathbf{G}'}(\mathbf{Q},z')\ , \tag{87}$$

or more concisely, as

$$\mathbf{D}_{\mathbf{G}}=\sum_{\mathbf{G}'}\hat{\epsilon}_{\mathbf{G}\mathbf{G}'}\mathbf{E}_{\mathbf{G}'}\ , \tag{88}$$

where $\hat{\epsilon}_{\mathbf{G}\mathbf{G}'}$ is an integral operator represented by

$$\overleftrightarrow{\epsilon}_{\mathbf{G}\mathbf{G}'}(\mathbf{Q},z,z')=\frac{1}{A}\int_0 d^2r_{\parallel}\int_0 d^2r'_{\parallel}\sum_{\mathbf{X}}\overleftrightarrow{\epsilon}(\mathbf{r}_{\parallel}+\mathbf{X},z,\mathbf{r}'_{\parallel}+\mathbf{X},z')e^{-i[(\mathbf{Q}+\mathbf{G})\cdot(\mathbf{r}_{\parallel}+\mathbf{X})-(\mathbf{Q}+\mathbf{G}')\cdot\mathbf{r}'_{\parallel}]}\ . \tag{89}$$

The longitudinal projector in the representation is given by

$$\hat{P}^{\mathrm{L}}_{\mathbf{G}\mathbf{G}'}=\delta_{\mathbf{G}\mathbf{G}'}\hat{\nabla}_{\mathbf{G}}\hat{\nabla}_{\mathbf{G}}^{-2}\hat{\nabla}_{\mathbf{G}}\ , \tag{90}$$

where $\hat{\nabla}_{\mathbf{G}}$ is the differential operator

$$\nabla_{\mathbf{G}}=\left[i(\mathbf{Q}+\mathbf{G}),\frac{\partial}{\partial z}\right]\ , \tag{91}$$

and $\hat{\nabla}_{\mathbf{G}}^{-2}$ is an integral operator represented by the function

$$\hat{\nabla}_{\mathbf{G}}^{-2}(z,z')=-\frac{1}{2}\frac{1}{|\mathbf{Q}+\mathbf{G}|}e^{-|\mathbf{Q}+\mathbf{G}|\,|z-z'|}\ . \tag{92}$$

In order to eliminate the fluctuations along the surface, we choose as an averaging procedure a truncation that eliminates all wave vectors outside of the first 2D Brillouin zone, so that $\hat{P}_a$ is represented by

$$(P_a)_{\mathbf{G}\mathbf{G}'}(\mathbf{Q},z,z')=\delta_{\mathbf{G}0}\delta_{\mathbf{G}'0}\delta(z-z')\ . \tag{93}$$

Then Eqs. (1)—(4) yield immediately

$$\hat{\epsilon}_m=\hat{\epsilon}_{00}-\sum_{\mathbf{G},\mathbf{G}'\,(\neq 0)}\hat{\epsilon}_{0\mathbf{G}}(\hat{\epsilon}_r^{\mathrm{LL}})^{-1}_{\mathbf{G}\mathbf{G}'}\hat{\epsilon}_{\mathbf{G}'0}\,, \tag{94}$$

$$\hat{\epsilon}_m^{-1}=\hat{\epsilon}_{00}^{-1}-\sum_{\mathbf{G},\mathbf{G}'\,(\neq 0)}\hat{\epsilon}_{0\mathbf{G}}^{-1}[(\hat{\epsilon}^{-1})_r^{\mathrm{TT}}]^{-1}_{\mathbf{G}\mathbf{G}'}\hat{\epsilon}_{\mathbf{G}'0}^{-1}\,, \tag{95}$$

$$(\hat{\epsilon}_m^{\mathrm{LL}})^{-1}=(\hat{\epsilon}^{\mathrm{LL}})_{00}^{-1}\,, \tag{96}$$

$$[(\hat{\epsilon}_m^{-1})^{\mathrm{TT}}]^{-1}=[(\hat{\epsilon}^{-1})^{\mathrm{TT}}]_{00}^{-1}\,, \tag{97}$$

where the caret over a symbol indicates that it represents an integral operator acting on the z coordinate, and the subscript r in $(\hat{\epsilon}_r^{\mathrm{LL}})^{-1}_{\mathbf{G}\mathbf{G}'}$ and $[(\hat{\epsilon}^{-1})_r^{\mathrm{TT}}]^{-1}_{\mathbf{G}\mathbf{G}'}$ is meant as a reminder to restrict the matrices $\hat{\epsilon}^{\mathrm{LL}}_{\mathbf{G}\mathbf{G}'}$ and $(\hat{\epsilon}^{-1})^{\mathrm{TT}}_{\mathbf{G}\mathbf{G}'}$ to reciprocal wave vectors $\mathbf{G},\mathbf{G}'\neq 0$ before attempting the matrix inversions. Here we used a lower case m instead of an upper case M as a subscript to denote the dielectric response given in Eqs. (94)—(97) because these are not truly macroscopic operators; they still have spatial fluctuations along the z direction. However, if we average Maxwell's equations with the projector (93) and then use Eqs. (94)—(97), we reduce the problem of the wave propagation through a 3D bounded crystal to the solution of an integrodifferential equation in just one variable. This might be susceptible to solution by numerical methods in systems such as thin films.[23]

A different approach is to also average out the fluctuations in the z direction by using a cutoff wave vector k_c. For this purpose, we take the Fourier transform of Eq. (87) along the z coordinate to write it as

$$\mathbf{D}_{\mathbf{G}}(\mathbf{Q},q)=\sum_{\mathbf{G}'}\int_{-\infty}^{\infty}\frac{dq'}{2\pi}\overleftrightarrow{\epsilon}_{\mathbf{G}\mathbf{G}'}(\mathbf{Q},q,q')\mathbf{E}_{\mathbf{G}'}(\mathbf{Q},q')\,, \tag{98}$$

where the fields are transformed according to

$$\mathbf{E}_{\mathbf{G}}(\mathbf{Q},z)=\int_{-\infty}^{\infty}\frac{dq'}{2\pi}e^{iqz}\mathbf{E}_{\mathbf{G}}(\mathbf{Q},q)\,, \tag{99}$$

and the operators are transformed according to

$$\overleftrightarrow{\epsilon}_{\mathbf{G}\mathbf{G}'}(\mathbf{Q},z,z')=\int_{-\infty}^{\infty}\frac{dq}{2\pi}\int_{-\infty}^{\infty}\frac{dq'}{2\pi}e^{i(qz-q'z')}\overleftrightarrow{\epsilon}_{\mathbf{G}\mathbf{G}'}(\mathbf{Q},q,q')\,. \tag{100}$$

The longitudinal projector is given by

$$\overleftrightarrow{P}^{\mathrm{L}}_{\mathbf{G}\mathbf{G}'}(\mathbf{Q},q,q')=2\pi\delta(q-q')\delta_{\mathbf{G}\mathbf{G}'}\frac{(\mathbf{G}+\mathbf{Q},q)(\mathbf{G}+\mathbf{Q},q)}{Q^2+q^2}\,, \tag{101}$$

and our choice of average projector is

$$(P_a)_{\mathbf{G}\mathbf{G}'}(\mathbf{Q},q,q')=2\pi\delta(q-q')\delta_{\mathbf{G}0}\delta_{\mathbf{G}'0}\Theta(k_c-q)\,, \tag{102}$$

where Θ is the usual step function. In order to eliminate the spatial fluctuations due to the atomic structure of the crystal, the cutoff wave vector k_c should obey the inequality

$$\frac{\omega}{c}\ll k_c<\frac{2\pi}{a}\,, \tag{103}$$

where a is the spatial period along the z direction in the bulk of the crystal. Now, Eqs. (11)—(14) become

$$\overleftrightarrow{\epsilon}_M(\mathbf{Q},q,q')=\overleftrightarrow{\epsilon}_{00}(\mathbf{Q},q,q')-\sum_{\mathbf{G},\mathbf{G}'\,(\neq 0)}\int_f\frac{dq''}{2\pi}\int_f\frac{dq'''}{2\pi}\overleftrightarrow{\epsilon}_{0\mathbf{G}}(\mathbf{Q},q,q'')(\overleftrightarrow{\epsilon}_r^{\mathrm{LL}})^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{Q},q'',q''')\overleftrightarrow{\epsilon}_{\mathbf{G}'0}(\mathbf{Q},q''',q')\,, \tag{104}$$

$$\overleftrightarrow{\epsilon}_M^{-1}(\mathbf{Q},q,q')=\overleftrightarrow{\epsilon}_{00}^{-1}(\mathbf{Q},q,q')-\sum_{\mathbf{G},\mathbf{G}'\,(\neq 0)}\int_f\frac{dq''}{2\pi}\int_f\frac{dq'''}{2\pi}\overleftrightarrow{\epsilon}_{0\mathbf{G}}^{-1}(\mathbf{Q},q,q'')[(\overleftrightarrow{\epsilon}^{-1})_r^{\mathrm{TT}}]^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{Q},q'',q''')\overleftrightarrow{\epsilon}_{\mathbf{G}',0}^{-1}(\mathbf{Q},q''',q')\,, \tag{105}$$

$$(\overleftrightarrow{\epsilon}_M^{\mathrm{LL}})^{-1}(\mathbf{Q},q,q')=(\overleftrightarrow{\epsilon}^{\mathrm{LL}})_{00}^{-1}(\mathbf{Q},q,q')\,, \tag{106}$$

$$[(\overleftrightarrow{\epsilon}_M^{-1})^{\mathrm{TT}}]^{-1}(\mathbf{Q},q,q')=[(\overleftrightarrow{\epsilon}^{-1})^{\mathrm{TT}}]_{00}^{-1}(\mathbf{Q},q,q')\,. \tag{107}$$

The subscript f under the integral sign $\int_f dq''/2\pi$ means that the wave vectors $q<k_c$ are to be excluded, and the subscript r under the dielectric operators is to restrict these to the subspace of fluctuating fields [those $F_{\mathbf{G}}(\mathbf{q})$ with $\mathbf{G}\neq\mathbf{0}$ and $q>k_c$] before attempting the required inversions. Equation (104) has been recently obtained and discussed by Del Sole.[24]

In order to get some insight about the macroscopic response near the surface of a crystal, we will follow still another approach. We will show an averaging procedure in real space with which we obtain from Eqs. (94) and (95) a dielectric response that (i) has no spatial fluctuations due to the atomic structure of the crystal, (ii) coincides with the bulk macroscopic response far from the surface, and (iii) gives the correct optical properties of the system.

First of all we investigate the relation between $\hat{\epsilon}_m$, $\hat{\epsilon}_m^{-1}$, and the bulk macroscopic response. We notice that in an infinite crystal, expressions (94) and (95) yield a dielectric response that corresponds to a system with full translational symmetry in the x-y plane and periodicity in the z direction, i.e.,

$$\overleftrightarrow{\epsilon}_m(z+Z,z'+Z)=\overleftrightarrow{\epsilon}_m(z,z')\,, \tag{108}$$

where $Z=na$ $(n=0,\pm1,\pm2,\ldots)$ forms a one-dimensional (1D) periodic lattice with lattice parameter a. The procedure followed in the preceding section can be easily modified to be used in a 1D lattice, and it gives the following expression for the macroscopic dielectric response:

$$\overleftrightarrow{\epsilon}_M=(\overleftrightarrow{\epsilon}_m)_{00}-\sum_{g,g'\,(\neq 0)}(\overleftrightarrow{\epsilon}_m)_{0g}[(\overleftrightarrow{\epsilon}_m)_r^{\mathrm{LL}}]^{-1}_{gg'}(\overleftrightarrow{\epsilon}_m)_{g'0}\,, \tag{109}$$

$$\overleftrightarrow{\epsilon}_M^{-1}=(\overleftrightarrow{\epsilon}_m^{-1})_{00}-\sum_{g,g'\,(\neq 0)}(\overleftrightarrow{\epsilon}_m^{-1})_{0g}[(\overleftrightarrow{\epsilon}_m^{-1})_r^{\mathrm{TT}}]_{gg'}^{-1}(\overleftrightarrow{\epsilon}_m^{-1})_{g'0}\,, \tag{110}$$

where g are wave vectors in a 1D reciprocal lattice, obtained by projecting on the z axis the 3D bulk reciprocal wave vectors. The notation should be clear from that used in Sec. IV. A cumbersome algebra shows that Eqs. (109) and (110), together with Eqs. (94) and (95), are equivalent to the expressions (74) and (75) for the macroscopic response found in the preceding section.

To simplify the following discussion we will ignore the nondiagonal components of $\overleftrightarrow{\epsilon}_m$ and we will make expansions of all quantities to the lowest possible order in Qa. Since g and g' point along the z direction, and since $g,g'\gg Q$, the xx and yy components of any longitudinal-longitudinal operator (such as $[(\overleftrightarrow{\epsilon}_m)_r^{\mathrm{LL}}]_{gg'}^{-1}$) are negligible, compared to its zz component. The opposite happens to transverse-transverse operators. Then Eqs. (109) and (110) yield immediately

$$\epsilon_M^{xx}=(\epsilon_m^{xx})_{00} \tag{111}$$

and

$$(\epsilon_M^{-1})^{zz}=(\epsilon_m^{-1})_{00}^{zz}\,, \tag{112}$$

which can be written as

$$\epsilon_M^{xx}(z-z')=\frac{1}{a}\int_{-a/2}^{a/2}dz''\int_{-\infty}^{\infty}dz'''\,\epsilon_m^{xx}(z+z'',z''+z''')w(z'''-z') \tag{113}$$

and

$$(\epsilon_M^{-1})^{zz}(z-z')=\frac{1}{a}\int_{-a/2}^{a/2}dz''\int_{-\infty}^{\infty}dz'''(\epsilon_m^{-1})^{zz}(z+z'',z''+z''')w(z'''-z')\,, \tag{114}$$

by transforming back to real space, where

$$w(z)=\int_{-\pi/a}^{\pi/a}\frac{dq}{2\pi}e^{iqz}=\frac{\sin(\pi z/a)}{\pi z} \tag{115}$$

is a normalized weight function. Thus, to obtain the macroscopic response in the bulk, we just have to perform a spatial average of ϵ_m^{xx} and $(\epsilon_m^{-1})^{zz}$.

Now we recall that Gauss's and Faraday's laws imply that when we average out the fluctuations of E^x and D^z along the x-y plane we obtain fields that also vary slowly in the z direction, even near the crystal's surface. Then we can replace the responses to these fields, ϵ_m^{xx} and $(\epsilon_m^{-1})^{zz}$, with their spatial averages without modifying the optical properties of the system (a formal proof of this statement is given in the Appendix). For this reason we define the macroscopic response for all z and z' as the average

$$\epsilon_M^{xx}(z,z')=\frac{1}{a}\int_{-a/2}^{a/2}dz''\int_{-\infty}^{\infty}dz'''\,\epsilon_m^{xx}(z+z'',z''+z''')w(z'''-z')\,, \tag{116}$$

$$(\epsilon_M^{-1})^{zz}(z,z')=\frac{1}{a}\int_{-a/2}^{a/2}dz''\int_{-\infty}^{\infty}dz'''(\epsilon_m^{-1})^{zz}(z+z'',z''+z''')w(z'''-z')\,. \tag{117}$$

Taking into account that E_0^x and D_0^z are slowly varying, we can ignore the spatial average with weight function w in expressions (153)—(157) and use instead the simplified expressions

$$\epsilon_M^{xx}(z,z')=\frac{1}{a}\int_{-a/2}^{a/2}dz''\,\epsilon_m^{xx}(z+z'',z'+z'') \tag{118}$$

and

$$(\epsilon_M^{-1})^{zz}(z,z')=\frac{1}{a}\int_{-a/2}^{a/2}dz''(\epsilon_m^{-1})^{zz}(z+z'',z'+z'')\,. \tag{119}$$

Clearly, ϵ_M^{xx} and $(\epsilon_M^{-1})^{zz}$, as defined in these equations, coincide with the bulk response, as given by Eqs. (113) and (114), when z and z' go away from the surface. Therefore, the optical properties of a crystal can now be calculated taking into account the local-field effect in the vicinity of its surface, using a perturbative approach such as the one developed in Ref. 54, where the perturbation parameter is the width of the region where the macroscopic response differs from its bulk value, divided by the wavelength of light.

VI. CONCLUSIONS

In this paper we have applied the general local-field-effect formalism developed in Ref. 1 to diverse systems of physical interest. Thus we obtained in a unified way the first corrections to the Clausius-Mossotti expression for the dielectric response of a liquid, expressions for the change in the ellipsometric coefficients, reflection amplitude, and reflectance, and for the change in the surface-plasmon—polariton dispersion relation of a semi-infinite system upon the roughening of its surface, the bulk dielectric tensor and the dispersion relation of the electromagnetic modes of an infinite crystal, and expressions for the macroscopic response near the surface of a crystal, which can be used in perturbative calculations of its optical properties. For the first two systems simple models of the microscopic response were used; for the infinite and semi-infinite crystals no specific model was introduced, but we took advantage of their periodicity. To perform actual calculations on crystals the microscopic response must be obtained first, either from a point-charge[16] or point-polarizable atom model,[3,17–21] or from a microscop-

ic Hamiltonian[22–26] using linear-response theory. Although some of our results are new, such as Eqs. (94)–(97), (116), and (117), most of them have been derived before by other workers using different techniques. However, the purpose of these calculations was to show explicitly the generality of the formalism as well as to explore its potential as a computational tool. The way we approach the problem offers for the first time a unified view of the local-field effect, and it can be followed in more elaborate models of spatially fluctuating systems. This will be the object of future research. This formalism also offers a point of view which might be complementary to the usual one, such as our treatment of the optical properties of rough surfaces in terms of the surface local-field effect.

ACKNOWLEDGMENTS

We want to thank R. Del Sole for communicating to us his results prior to publication, and A. Bagchi, R. Fuchs, and E. Martina for very fruitful discussions.

APPENDIX

Using our general local-field-effect theory we have shown that the optical properties of a semi-infinite crystal with microscopic response $\overleftrightarrow{\epsilon}(\mathbf{r},\mathbf{r}')$ are the same as the optical properties of a system with the response $\overleftrightarrow{\epsilon}_m(z,z')$ given by Eq. (94). This response has microscopic fluctuations along the z direction. We will show below that a system with dielectric function $\overleftrightarrow{\epsilon}_M(z,z')$ as given by Eq. (113), and therefore with no microscopic fluctuations, has the same optical properties. We consider only the case of p-polarized light, since the s-polarized case is similar.

We start by writing Maxwell's equations for the latter system in integral form as[54]

$$E^x=E_v^x-\frac{\omega^2}{c^2}\hat{G}^{xx}\Delta\hat{\epsilon}_M^{xx}E^x+\frac{\omega^2}{c^2}\hat{G}^{xz}\Delta(\hat{\epsilon}_M^{-1})^{zz}D^z\,, \tag{A1}$$

$$D^z=E_v^z-\frac{\omega^2}{c^2}\hat{G}^{zx}\Delta\hat{\epsilon}_M^{xx}E^x+\frac{\omega^2}{c^2}(\hat{G}')^{zz}\Delta(\hat{\epsilon}_M^{-1})^{zz}D^z\,, \tag{A2}$$

where $\hat{G}$ is the electromagnetic Green's function of vacuum which obeys

$$\left[\hat{1}\left[\nabla^2+\frac{\omega^2}{c^2}\right]-\nabla\nabla\cdot\right]\hat{G}=\hat{1}\,, \tag{A3}$$

$$(\hat{G}')^{zz}\equiv\hat{G}^{zz}-\frac{c^2}{\omega^2}\hat{1}\,, \tag{A4}$$

E_v^x and E_v^z are the x and z components of the external field,

$$\Delta\hat{\epsilon}_M^{xx}\equiv\hat{\epsilon}_M^{xx}-\hat{1}\,, \tag{A5}$$

$$\Delta(\hat{\epsilon}_M^{-1})^{zz}\equiv(\hat{\epsilon}_M^{-1})^{zz}-\hat{1}\,, \tag{A6}$$

and E^x and D^z are averaged along the x-y plane, and are therefore slowly varying in the z direction.

Using Eqs. (116) and (117) we find in Eqs. (A1) and (A2) integrals such as

$$I(z)=\frac{1}{a}\int_{-\infty}^{\infty}dz'\int_{-\infty}^{\infty}dz''\int_{-\infty}^{\infty}dz'''\int_{-a/2}^{a/2}dz''''G^{xx}(z,z')\Delta\epsilon_m^{xx}(z'+z'''',z''''+z''')w(z'''-z'')E^x(z'')\,. \tag{A7}$$

Since E^x is slowly varying, its average using w leaves it unchanged, so that performing the integral over z'' we get

$$I(z)\approx\frac{1}{a}\int_{-\infty}^{\infty}dz'\int_{-\infty}^{\infty}dz'''\int_{-a/2}^{a/2}dz''''G^{xx}(z,z')\Delta\epsilon_m^{xx}(z'+z'''',z''''+z''')E^x(z''')\,. \tag{A8}$$

Since G^{xx} is also slowly varying, we can approximate $G^{xx}(z,z')\approx G^{xx}(z,z'+z'''')$ and $E^x(z''')\approx E^x(z'''+z'''')$ so that Eq. (A8) becomes

$$I(z)\approx\int_{-\infty}^{\infty}dz'\int_{-\infty}^{\infty}dz''G^{xx}(z,z')\Delta\epsilon_m^{xx}(z',z'')E^x(z'') \tag{A9}$$

after a simple change of variables.

Proceeding in a similar fashion with the outer terms of Eqs. (A1) and (A2), we finally obtain

$$E^x=E_v^x-\frac{\omega^2}{c^2}\hat{G}^{xx}\Delta\hat{\epsilon}_m^{xx}E^x+\frac{\omega^2}{c^2}\hat{G}^{xz}\Delta(\hat{\epsilon}_m^{-1})^{zz}D^z \tag{A10}$$

and

$$D^z=E_v^z-\frac{\omega^2}{c^2}\hat{G}^{zx}\Delta\hat{\epsilon}_m^{xx}E^x+\frac{\omega^2}{c^2}(\hat{G}')^{zz}\Delta(\hat{\epsilon}_m^{-1})^{zz}D^z\,, \tag{A11}$$

which are Maxwell's equations in integral form for a system with response $\hat{\epsilon}_m$. Therefore $\hat{\epsilon}_m$ and $\hat{\epsilon}_M$ lead to the same optical properties.

Notice that if expressions (118) and (119) were used instead of (116) and (117), we would have arrived at Eq. (A8) without going through Eq. (A7).

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