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LOCAL FIELDS NEAR THE SURFACE OF A CRYSTALLINE DIELECTRIC

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We calculate the variation of the local electric field with depth near the surface of a crystalline dielectric, for the cases of induced atomic dipoles oriented perpendicular and parallel to the surface. The crystalline dielectric is modelled by a cubic lattice of polarizable atoms, with the surface in the (001) plane. Our calculations show that the departure of the local field from its bulk value is confined almost entirely to the outermost plane, and even there is small (at the most a few percent).

1. Introduction

In this paper we shall study the variation with depth of the field polarizing the atoms within a dielectric (the local field, also known as the internal or effective field). Our motivation in this work comes from the study of the surface structure of liquids[1]). Current ellipsometric measurements[2]) of the interface thickness require for their interpretation a knowledge of the relationship between the dielectric functions $\epsilon_\perp(z)$ and $\epsilon_\parallel(z)$ and the number density $n(z)$ of the atoms constituting the fluid; or better, the dependence of the local field on $n(z)$. The theory for inhomogeneous fluids[3]) parallels the crystalline case discussed here, but is more complicated. The crystalline case, while not directly applicable to fluids, has an intrinsic interest of its own, and in addition its solution will be useful in the theory of reflection of light by solids (cf. Vlieger[4])).

The local field E^{loc} is fundamental in the microscopic theory of the electrical and optical properties of dielectrics, since it is the field which relates atomic dipole moment p to the atomic polarizability α

$$p = \alpha E^{\text{loc}}. \tag{1}$$

Lorentz[5]) [see also Nijboer and De Wette[6])] showed that inside a lattice with atoms on sites of cubic symmetry, and with the polarized atoms approximated by point dipoles, the local field is

$$E^{\text{loc}} = \frac{E^{\text{ext}}}{1 + (8/3)\pi n\alpha}, \tag{2}$$

where E^{ext} is the field due to charges outside the dielectric. This result leads to the Clausius–Mossotti expression for the bulk dielectric constant

$$\epsilon = \frac{1+(8/3)\pi n\alpha}{1-(4/3)\pi n\alpha}. \tag{3}$$

That the point-dipole approximation leads to very small errors in solids like argon can be seen by comparing (3) with experiment. For example, for solid argon near the triple point we have $n = 0.0245$ Å^{-3} (ref. 7, table II) and $\alpha = 1.62$ Å^3 (ref. 8, p. 80) which gives $\epsilon = 1.60$, in agreement with the experimental value[9]). (For a theoretical calculation of the effect of extended atomic charges, see Guertin and Stern[10]), and for the effect of higher multipole moments on the dielectric function, see McKenzie and McPhedran[11])). We shall thus assume that the atomic fields can be approximated by those of point dipoles. In the following sections we shall solve the self-consistency equation for the local field for two directions (perpendicular and parallel to the surface) of the alignment of the dipoles.

2. Dipoles aligned perpendicular to the surface

The system under consideration is shown schematically in fig. 1. The dielectric is a slab, N atomic layers thick, and extending to infinity in the $\pm x$ and $\pm y$-directions. It is placed between oppositely charged parallel plates; these provide the external field E^{ext}, oriented perpendicular to the surface. The self-consistency equation reads

$$E^{loc} = E^{ext} + E^{dip}, \tag{4}$$

where E^{loc} is the field defined by (1) acting on a particular atom, and E^{dip} is the field at the chosen atom due to all other atomic dipoles. All atoms at the same depth have the same local field. Thus we will refer to E_n^{loc}, meaning the local field experienced by an atom in the nth layer.

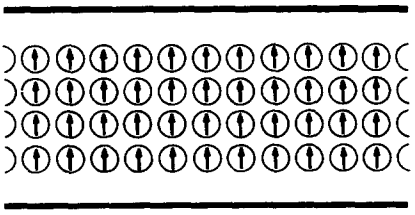

Fig. 1. System of dipoles aligned perpendicular to the surface.

The field at $r = r\hat{r}$ due to a dipole p at the origin is $r^{-3}[3(p \cdot \hat{r})\hat{r} - p]$. The only component of this field of interest here is that parallel to p (all the atomic dipoles are parallel in the cases we consider), the other components cancelling. The component parallel to p is $pr^{-3}[3(\hat{p} \cdot \hat{r})^2 - 1]$. Consider an atom in the nth layer of the cubic lattice, with coordinates $(0, 0, na)$. The p-component of the field on this atom from an atomic dipole centered on (la, ma, ka) is

$$\alpha E_k^{\text{loc}} a^{-3}\{l^2 + m^2 + (n-k)^2\}^{-3/2}\left[\frac{3(n-k)^2}{l^2 + m^2 + (n-k)^2} - 1\right], \tag{5}$$

since $\hat{p} = (0, 0, 1)$. The contribution from all the atomic dipoles in the kth layer is therefore

$$\frac{\alpha}{a^3} E_k^{\text{loc}} \sum_{l,m=-\infty}^{\infty}\sum \frac{2(n-k)^2 - (l^2 + m^2)}{\{l^2 + m^2 + (n-k)^2\}^{5/2}}. \tag{6}$$

Thus eq. (4) reads

$$E_n^{\text{loc}} = E^{\text{ext}} + \frac{\alpha}{a^3} \sum_{k=1}^{N} E_k^{\text{loc}} S_{n-k}, \tag{7}$$

where

$$S_n = \sum_{-\infty}^{\infty}\sum \frac{2n^2 - (l^2 + m^2)}{\{l^2 + m^2 + n^2\}^{5/2}}. \tag{8}$$

Note $S_n = S_{-n}$, and that the $l^2 + m^2 = 0$ term is excluded from S_0. These lattice sums are slowly convergent if evaluated directly[12]), but may be transformed to rapidly converging series, as detailed in Van der Hoff and Benson[13]). They give

$$S_0 = 4\zeta(2) + 2\zeta(3) + 16\pi \sum_1^{\infty}\sum_1^{\infty} \frac{l}{m} K_1(2\pi lm), \tag{9}$$

where K is a modified Bessel function of the second kind. For $n > 0$, S_n may be found from $\Sigma\,\Sigma_{-\infty}^{\infty}(l^2 + m^2 + n^2)^{-3/2}$, which we evaluate by the same method to be

$$\frac{2\pi}{n}\coth \pi n + \frac{8\pi}{n}\sum_1^{\infty} lK_1(2\pi ln) + 16\pi \sum_1^{\infty}\sum_1^{\infty} \frac{l}{\sqrt{m^2 + n^2}} K_1(2\pi l\sqrt{m^2 + n^2}).$$

We then find S_n from

$$S_n = -\left(1 + n\frac{\partial}{\partial n}\right)\sum_{-\infty}^{\infty}\sum (l^2 + m^2 + n^2)^{-3/2}. \tag{10}$$

This gives, for $n > 0$

$$S_n = \frac{2\pi^2}{\sinh^2 \pi n} + 8\pi \sum_1^\infty \frac{l}{n}\{2\pi l n K_2(2\pi l n) - K_1(2\pi l n)\} + 16\pi \sum_1^\infty \sum_1^\infty \frac{l}{\sqrt{m^2+n^2}}\left\{\frac{2\pi l n^2}{\sqrt{m^2+n^2}} K_2(2\pi l\sqrt{m^2+n^2}) - K_1(2\pi l\sqrt{m^2+n^2})\right\}. \quad (11)$$

The first four sums, rounded to seven decimals, are

$$S_0 = -9.0336217, \quad S_1 = 0.3274646, \quad S_2 = 0.0005550, \quad S_3 = 0.0000010. \quad (12)$$

For larger n, the first term in (11) is dominant, and successive sums decrease by the factor $e^{2\pi}$. (This is in accord with the known fact that the electric field from a periodic structure decreases exponentially with distance[14]).) S_0 is large and negative because all the dipolar fields in the same plane as a given atom oppose the external field at that atom; S_1 is much smaller because the five nearest dipoles in a neighbouring plane reinforce the external field, the next four have zero component, while the others oppose the external field; and so on.

Knowing the sums, we can solve the N linear simultaneous equations (7) exactly for small N. For a monolayer, (7) gives (cf. Vlieger[15]))

$$E_1^{\text{loc}} = \frac{E^{\text{ext}}}{1-(\alpha/a^3)S_0}. \quad (13)$$

For $N = 2$,

$$E_1^{\text{loc}} = E_2^{\text{loc}} = \frac{E^{\text{ext}}}{1-(\alpha/a^3)(S_0+S_1)}. \quad (14)$$

For larger or macroscopic N we need a different method. We first note that deep inside the solid, the local field tends to a constant, E_L^{loc}. Because of the rapid decrease of the S_n with n, (7) gives for E_L^{loc} the equation

$$E_L^{\text{loc}} = E^{\text{ext}} + \frac{\alpha}{a^3} E_L^{\text{loc}} \sum_{k=1}^N S_{n-k}. \quad (15)$$

In appendix A we show that

$$\sum_{k=1}^N S_{n-k} \to -\frac{8\pi}{3}, \quad (16)$$

provided that n, N and $N-n$ are "large" (actually it is sufficient to keep terms up to $|n-k| = 3$ for seven decimal place accuracy). Thus we regain the

Lorentz local field of eq. (2)

$$E_L^{loc} = \frac{E^{ext}}{1 + (8/3)\pi\alpha/a^3}. \tag{17}$$

For the variation of the local field near the surface, we shall first give an approximate solution, and then discuss the correction terms. Since $|S_0|$ is 27 times larger than S_1, the dominant contribution to the local field at an atom comes from the atomic dipoles in the same plane. This suggests approximating E_k^{loc} on the right side of (7) by E_n^{loc}; we obtain

$$E_n^{loc} \simeq \frac{E^{ext}}{1 - (\alpha/a^3)\sum_{k=1}^{N} S_{n-k}} \tag{18}$$

(the same form as (15) but n is now not restricted to large values). Thus

$$E_1^{loc} \simeq \frac{E^{ext}}{1 - (\alpha/a^3)(S_0 + S_1 + S_2 + \cdots)} = \frac{E^{ext}}{1 + (\alpha/a^3)((8\pi/3) + S_1 + S_2 + \cdots)},$$

$$E_2^{loc} \simeq \frac{E^{ext}}{1 - (\alpha/a^3)(S_0 + 2S_1 + S_2 + \cdots)} = \frac{E^{ext}}{1 + (\alpha/a^3)((8\pi/3) + S_2 + \cdots)} \tag{19}$$

and so on. As expected, the largest deviation from the Lorentz value is in the outermost layer. Using $\alpha/a^3 = 0.04$ (a cubic lattice with this parameter would have a bulk dielectric constant equal to that of solid argon, namely 1.6), we find $E_1^{loc} \simeq 0.99 E_L^{loc}$ and $E_2^{loc} \simeq 0.99998 E_L^{loc}$. Our preliminary conclusion is that the deviation of the local field (and thus of the dielectric function) from its bulk value will be non-negligible only in the outermost layer.

In appendix B we show that the lowest order correction to the approximate solution given above for E_k^{loc}/E_L^{loc} is of order $(\alpha/a^3)^2 S_1^2$ for $n = 1$ and 2, and zero to this order for $n \geq 3$. For the numerical example given above this is less than 2×10^{-4}.

3. Dipoles aligned parallel to the surface

The geometry used in this section is given schematically in fig. 2. The capacitor plates lie in y–z planes, providing an external field which orients the dipoles is the x-direction. The dielectric is of infinite depth but has a finite, though large, number of layers between the plates.

This case is complicated by the fact that the surface charge on the capacitor plates adjusts itself to the presence of the dielectric and therefore will depend on the depth, as does the dipole moment per unit volume. Not only will the external field vary with depth, but it will also fringe, that is have a component

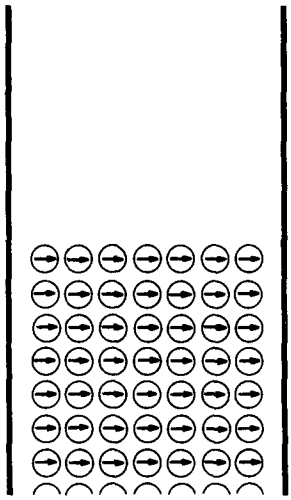

Fig. 2. System of dipoles aligned parallel to the surface.

in the z-direction, due to the non-uniformity in the surface charge density. In the following paper we discuss the fringing in more detail and show that the z-variation and fringing in the external field is cancelled exactly by equal and opposite effects in the field E^{dip} due to all the dipoles in the dielectric. Thus for this geometry, despite the behaviour of the external field, the dipoles align themselves with the average field, parallel to the surface. Analogous to (35) in the following paper, we have

$$E_n^{\text{loc}} = E^{\text{ave}} - \frac{1}{2}\frac{\alpha}{a^3}\sum_{k=1}^{\infty} E_k^{\text{loc}} S_{n-k}, \tag{20}$$

where E^{ave} is the average field given by

$$E^{\text{ave}} = E_{\text{bulk}}^{\text{ext}} - 4\pi\frac{\alpha}{a^3}E_{\text{L}}^{\text{loc}} = E_{\text{outside}}^{\text{ext}}. \tag{21}$$

$E_{\text{bulk}}^{\text{ext}}$ is the external field in the dielectric bulk and $E_{\text{outside}}^{\text{ext}}$ is the external field outside the dielectric and well away from the surface.

Since the sum in (20) is just $-\frac{1}{2}$ times the sum we had in (7), we can use the results of section 2 to immediately write down the corresponding results for this section. We first note that for n large, (20) becomes, using (16)

$$E_{\text{L}}^{\text{loc}} = E^{\text{ave}} + \frac{4}{3}\pi\frac{\alpha}{a^3}E_{\text{L}}^{\text{loc}}, \tag{22}$$

which, by (21) is

$$E_{\mathrm{L}}^{\mathrm{loc}} = \frac{E_{\mathrm{bulk}}^{\mathrm{ext}}}{1 + (8/3)\pi\alpha/a^3} \tag{23}$$

and so (20) does predict the Lorentz value for the local field inside the dielectric.

Under the approximation $E_k^{\mathrm{loc}} = E_n^{\mathrm{loc}}$, (20) and (16) give

$$\begin{aligned} E_n^{\mathrm{loc}} &\simeq \frac{E^{\mathrm{ave}}}{1 - (4/3)\pi\alpha/a^3 - \frac{1}{2}(\alpha/a^3)\sum_n^{\infty} S_k} \\ &= \frac{1 - (4/3)\pi\alpha/a^3}{1 + (8/3)\pi\alpha/a^3} \frac{E_{\mathrm{bulk}}^{\mathrm{ext}}}{1 - (4/3)\pi\alpha/a^3 - \frac{1}{2}(\alpha/a^3)\sum_n^{\infty} S_k}. \end{aligned} \tag{24}$$

Using $\alpha/a^3 = 0.04$ we get $E_1^{\mathrm{loc}} = 1.008E_{\mathrm{L}}$ and $E_2^{\mathrm{loc}} = 1.00001E_{\mathrm{L}}$. The deviation of these values from the bulk value is even smaller than it was for the perpendicular case. Corrections to (24) are of order 0.5×10^{-4} for the first and second layers.

Acknowledgements

We are indebted to John Kimbal for pointing out the general solution (B.3), and to Alan Portis and David Beaglehole for valuable discussions.

Appendix A

Proof of $\Sigma_{k=1}^{\infty} S_{n-k} \to -8\pi/3$ *for large* n

We shall prove this in the form

$$\sum_{-N}^{N} S_n \to -\frac{8\pi}{3} \tag{A.1}$$

for large N. We have, from (8), $S_n = \lim_{M\to\infty} S_n^M$, where

$$S_n^M = \sum_{-M}^{M}\sum_{-M}^{M} \frac{2n^2 - (l^2 + m^2)}{(l^2 + m^2 + n^2)^{5/2}}. \tag{A.2}$$

Now

$$\sum_{-N}^{N} S_n^M = \sum_{-M}^{M} S_n^M - 2\sum_{N+1}^{M} S_n^M, \tag{A.3}$$

for all $N < M$. The first sum is zero by symmetry, and the second we can replace by a triple integral, provided $N \gg 1$:

$$\begin{aligned}\sum_{N+1}^{M} S_n^M &\to 4 \int_N^M \mathrm{d}n \int_0^M \mathrm{d}l \int_0^M \mathrm{d}m \, \frac{3n^2-(l^2+m^2+n^2)}{(l^2+m^2+n^2)^{5/2}} \\ &= -4 \int_N^M \mathrm{d}n \int_0^M \mathrm{d}l \int_0^M \mathrm{d}m \left(1+n\frac{\partial}{\partial n}\right)(l^2+m^2+n^2)^{-3/2} \\ &= 4 \int_0^M \mathrm{d}l \int_0^M \mathrm{d}m \left[\frac{N}{(l^2+m^2+N^2)^{3/2}} - \frac{M}{(l^2+m^2+M^2)^{3/2}}\right] \\ &= 4\left\{J\left(\frac{N}{M}\right) - J(1)\right\},\end{aligned} \tag{A.4}$$

where

$$J(\lambda) = \int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}y \, \frac{\lambda}{(x^2+y^2+\lambda^2)^{3/2}} = \frac{\pi}{2} - 2\arcsin\frac{\lambda}{\sqrt{2\lambda^2+2}}. \tag{A.5}$$

The last result is obtained by changing to polar coordinates and using

$$\int_0^{\pi/4} \mathrm{d}\theta \, \frac{\lambda}{\sqrt{\lambda^2+\sec^2\theta}} = \arcsin\frac{\lambda}{\sqrt{2\lambda^2+2}}. \tag{A.6}$$

For the capacitor geometry of fig. 1, $N/M \to 0$, so (A.3) and (A.4) give

$$\lim_{M\to\infty} \sum_{-N}^{N} S_n^M = -8\left\{\frac{\pi}{2} - \left(\frac{\pi}{2} - 2\arcsin\frac{1}{2}\right)\right\} = -\frac{8\pi}{3}. \tag{A.7}$$

Appendix B

Evaluation of correction terms

The system of N coupled linear equations for E_n^{loc}, eq. (7), can be written as

$$f_n = 1 + \sum_{k=1}^{N} A_{nk} f_k, \tag{B.1}$$

where $f_n = E_n^{\mathrm{loc}}/E^{\mathrm{ext}}$, and $A_{nk} = (\alpha/a^3)S_{n-k} = A_{kn}$. In matrix form,

$$(I - A)f = \mathbf{1}, \tag{B.2}$$

where I is the unit matrix and $\mathbf{1}$ a vector of 1's. Provided that the largest eigenvalue of A has modulus less than unity, the general solution of (B.2) is

$$f = (I - A)^{-1}\mathbf{1} = \mathbf{1} + A\mathbf{1} + A^2\mathbf{1} + \cdots, \tag{B.3}$$

or

$$f_n^{\text{exact}} = 1 + \sum_{k=1}^{N} A_{nk} + \sum_{k=1}^{N}\sum_{l=1}^{N} A_{nl}A_{lk} + \cdots. \tag{B.4}$$

Our approximate solution (18) can be written as

$$f_n^{\text{approx}} = \frac{1}{1 - \sum_{k=1}^{N} A_{nk}} = 1 + \sum_{k=1}^{N} A_{nk} + \sum_{k=1}^{N}\sum_{l=1}^{N} A_{nk}A_{nl} + \cdots. \tag{B.5}$$

Thus

$$f_n^{\text{exact}} - f_n^{\text{approx}} = \sum_{k=1}^{N}\sum_{l=1}^{N} (A_{lk} - A_{nk})A_{nl} + \mathcal{O}\left(\frac{\alpha}{a^3}\right)^3. \tag{B.6}$$

Define

$$\begin{aligned} B_{ln} &= \sum_{k=1}^{N} (A_{lk} - A_{nk}) = -B_{nl} \\ &= \frac{\alpha}{a^3}\sum_{k=1}^{N} (S_{k-l} - S_{k-n}) \\ &= \frac{\alpha}{a^3}\left\{\sum_{1-l}^{N-l} S_\lambda - \sum_{1-n}^{N-n} S_\lambda\right\}. \end{aligned} \tag{B.7}$$

When N is much larger than n or l, this reduces to

$$B_{ln} = \frac{\alpha}{a^3}\,\mathrm{sgn}(l - n)\sum_{\min(l,n)}^{\max(l,n)-1} S_\lambda, \tag{B.8}$$

i.e.

$$B = \frac{\alpha}{a^3}\begin{pmatrix} 0 & -S_1 & -(S_1+S_2) & -(S_1+S_2+S_3) & \cdots \\ S_1 & 0 & -S_2 & -(S_2+S_3) & \cdots \\ S_1+S_2 & S_2 & 0 & -S_3 & \cdots \\ S_1+S_2+S_3 & S_2+S_3 & S_3 & 0 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \ddots \end{pmatrix} \tag{B.9}$$

From (B.6)

$$f_n^{\text{exact}} - f_n^{\text{approx}} = \sum_{l} B_{ln}A_{nl} + \mathcal{O}\left(\frac{\alpha}{a^3}\right)^3. \tag{B.10}$$

Thus, to $\mathcal{O}(\alpha/a^3)^2$,

$$f^{\text{exact}} - f^{\text{approx}} = \left(\frac{\alpha}{a^3}\right)^2 \begin{pmatrix} S_1^2 + (S_1+S_2)S_2 + (S_1+S_2+S_3)S_3 + \cdots \\ -S_1^2 + S_1S_2 + (S_2+S_3)S_2 + \cdots \\ -(S_1+S_2)S_2 - S_2S_1 + S_3S_1 + \cdots \\ -(S_1+S_2+S_3)S_3 - (S_2+S_3)S_2 - S_3S_1 + \cdots \\ \cdots\cdots \end{pmatrix}. \quad \text{(B.11)}$$

The leading correction terms are therefore given by

$$f^{\text{exact}} - f^{\text{approx}} \simeq \left(\frac{\alpha}{a^3}\right)^2 \begin{pmatrix} S_1^2 \\ -S_1^2 \\ 0 \\ 0 \\ \vdots \end{pmatrix}. \quad \text{(B.12)}$$

The case of dipoles oriented parallel to the surface is similar to the above, with $-\frac{1}{2}S_n$ replacing S_n.

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