Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

To cite this article: Ulderico Segre (1983): Cavity and Reaction Fields in Anisotropic Dielectrics, Molecular Crystals and Liquid Crystals, 90:3-4, 239-244

To link to this article: http://dx.doi.org/10.1080/00268948308072452

Mol. Cryst. Liq. Cryst., 1983, Vol. 90, pp. 239–244
0026-8941/83/9004–0239$18.50/0

Printed in the United States of America

Cavity and Reaction Fields in Anisotropic Dielectrics

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(*Received July 20, 1982*)

An ellipsoidal cavity arbitrarily oriented in an anisotropic dielectric is considered. The cavity field and the reaction field (for an homogeneous dipole density) inside the cavity are computed, and the general expressions are compared with those obtained by previous authors for particular geometries. The average local field acting on a molecule in non-polar liquid crystals is found to be linearly dependent upon the orientational degree of order.

INTRODUCTION

In the last years some interest has been devoted to the problem of the electric field inside a cavity surrounded by an anisotropic dielectric, e.g., a liquid crystal.[1-9]

Following Onsager[10] the computation is divided in two steps: first, the expression for the field inside the empty cavity is obtained, in the presence of an homogeneous external field; then the cavity field is corrected for the reaction due to the induced or permanent molecular dipole moments. For a spherical cavity in an anisotropic dielectric, the solution to the first problem is well known,[11] while an expression for the reaction field has been reported without proof by Kuznetsov *et al.*[5] More recently, the case of an ellipsoidal cavity whose axes are coincident with the principal directions of the permittivity tensor has been considered, but two different expressions for the reaction field have been obtained.[8,9]

The aim of this paper is to solve the Onsager problem for the general case of an ellipsoidal cavity with arbitrary orientation with respect to the permittivity principal axes. Some years ago Derzhanski and Petrov[2]

tackled this problem as well, but it seems that they did not consider correctly the tensorial properties of the permittivity, and their results are incorrect for a spherical cavity. The general solution of the cavity problem which is obtained in the following includes the particular cases treated previously, and therefore discriminates between conflicting expressions.

THEORY

An ellipsoidal cavity with semi-axes (a_1, a_2, a_3) is surrounded by an anisotropic homogeneous dielectric. The principal axes of the ellipsoid and of the permittivity ε are supposed to be non-coincident, and $\Omega = (\alpha, \beta, \gamma)$ is the set of Euler angles relating the two frames.[12] An external electric field $\mathbf{E}_0$ is applied, which is supposed to be uniform at very large distances from the cavity.

Cavity field

The electric field inside the empty cavity is obtained by solving the equations for the potential inside and outside the cavity:

$$\Sigma_j \frac{\partial^2 \phi^{(i)}}{\partial x_j^2} = 0 \tag{1}$$

$$\Sigma_j \epsilon_j \frac{\partial^2 \phi^{(e)}}{\partial x_j^2} = 0 \tag{2}$$

where the permittivity principal axes are chosen as the reference frame. The link between the internal and external solutions is given by the usual continuity conditions,[11] which are to be satisfied on the ellipsoidal surface, whose analytical equation is:

$$\Sigma_{ij} x_i M_{ij} x_j = 1 \tag{3}$$

$$M_{ij} = \Sigma_k R_{ik} (1/a_k^2) R_{jk} \tag{4}$$

where $R_{jk}(\alpha, \beta, \gamma)$ are the components of the Euler matrix. This problem can be solved by a coordinate transformation:

$$x_i = (\epsilon_i)^{1/2} x_i' \tag{5}$$

With respect to the new variables, Eqs. (1–4) become:

$$\Sigma_j \epsilon_j^{-1} \frac{\partial^2 \phi^{(i)}}{\partial x_j'^2} = 0 \tag{6}$$

$$\Sigma_j \frac{\partial^2 \phi^{(e)}}{\partial x_j'^2} = 0 \tag{7}$$

$$\Sigma_{ij} x_i' M_{ij}' x_j' = 1 \tag{8}$$

$$M_{ij}' = (\epsilon_i \epsilon_j)^{1/2} M_{ij} \tag{9}$$

Now we deal with the completely equivalent problem of the internal field for an ellipsoidal body *in vacuo*, composed of an anisotropic dielectric with permittivity $\boldsymbol{\varepsilon}' = \boldsymbol{\varepsilon}^{-1}$. The shape of the ellipsoidal body, as well as its orientation, are different from those of the cavity in the initial problem. The values of the semi-axes and direction cosines are found by diagonalizing the matrix $\mathbf{M}'$. The electric field $\mathbf{E}'^{(i)}$ inside this body is given by:[11]

$$\mathbf{E}'^{(i)} = \{1 + \mathbf{n}'(\boldsymbol{\varepsilon}' - 1)\}^{-1} \mathbf{E}_0' \tag{10}$$

where $\mathbf{n}'$ is its depolarization tensor, and $\mathbf{E}_0' = \boldsymbol{\varepsilon}^{1/2} \mathbf{E}_0$. Reverting to the original coordinates we find the expression for the cavity field:

$$\begin{aligned} \mathbf{E}_c &= \mathbf{g} \cdot \mathbf{E}_0 \\ &= \boldsymbol{\varepsilon}^{1/2} \{\boldsymbol{\varepsilon} - \mathbf{n}'(\boldsymbol{\varepsilon} - 1)\}^{-1} \boldsymbol{\varepsilon}^{1/2} \mathbf{E}_0 \end{aligned} \tag{11}$$

It is worth noting that $\mathbf{n}'$ is different from $\mathbf{n}$, the depolarization tensor of the ellipsoidal cavity, and that $\mathbf{n}'$, $\mathbf{n}$ and $\boldsymbol{\varepsilon}$ in general do not commute, unless $\boldsymbol{\Omega} = (0, 0, 0)$. In this particular case the expression for the cavity tensor $\mathbf{g}$ previously reported[8,9] is recovered.

Reaction field

If the cavity is filled up by an homogeneous dipole density, with dielectric permittivity ϵ_i, the field inside the cavity is modified by the reaction field $\mathbf{E}_r = \mathbf{f}\,\mathbf{m}$ due to the polarization of the environment. The dipole moment of the ellipsoid is related to the internal field by:[13]

$$\begin{aligned} \mathbf{m} &= (V/4\pi)(\epsilon_i - 1)\mathbf{E}_i \\ &= (V/4\pi)(\epsilon_i - 1)\boldsymbol{\varepsilon}^{1/2} \{\boldsymbol{\varepsilon} - \mathbf{n}'(\boldsymbol{\varepsilon} - \epsilon_i)\}^{-1} \boldsymbol{\varepsilon}^{1/2} \mathbf{E}_0 \end{aligned} \tag{12}$$

On the other hand, if $\boldsymbol{\alpha} = (V/4\pi)(\epsilon_i - 1)\{1 + \mathbf{n}(\epsilon_i - 1)\}^{-1}$ is the polarizability of the ellipsoid, we have:

$$\mathbf{m} = \boldsymbol{\alpha} \cdot (\mathbf{E}_c + \mathbf{E}_r) = \boldsymbol{\alpha} \cdot (\mathbf{g} \cdot \mathbf{E}_0 + \mathbf{f} \cdot \mathbf{m}) \tag{13}$$

Therefore, after some algebra, we obtain:

$$\begin{aligned} \mathbf{f} = (4\pi/V)\boldsymbol{\varepsilon}^{1/2} &\{\boldsymbol{\varepsilon} - \mathbf{n}'(\boldsymbol{\varepsilon} - 1)\}^{-1} \\ &\{(1 - \mathbf{n}')\boldsymbol{\varepsilon}\mathbf{n}'' - \mathbf{n}'(1 - \mathbf{n}'')\}\boldsymbol{\varepsilon}^{-1/2} \end{aligned} \tag{14}$$

where $\mathbf{n}'' = \boldsymbol{\varepsilon}^{-1/2}\mathbf{n}\boldsymbol{\varepsilon}^{1/2}$. When $\Omega = (0, 0, 0)$, all the tensors involved in Eq. (14) commute, and the reaction tensor becomes:

$$\mathbf{f} = (4\pi/V)\{\boldsymbol{\varepsilon} - \mathbf{n}'(\boldsymbol{\varepsilon} - 1)\}^{-1}\{\mathbf{n}(1 - \mathbf{n}')\boldsymbol{\varepsilon} - \mathbf{n}'(1 - \mathbf{n})\} \tag{15}$$

We recall that in Eq. (15) $\mathbf{n}$ is the depolarization tensor of the ellipsoid with semi-axes (a_1, a_2, a_3), while $\mathbf{n}'$ is the depolarization tensor of the ellipsoid with semi-axes $(a_1/\sqrt{\epsilon_1}, a_2/\sqrt{\epsilon_2}, a_3/\sqrt{\epsilon_3})$. In the case of a spherical cavity we have $\mathbf{n} = 1/3$, and Eq. (15) becomes:

$$\mathbf{f} = \{\boldsymbol{\varepsilon} - \mathbf{n}'(\boldsymbol{\varepsilon} + 2)\}\{\boldsymbol{\varepsilon} - \mathbf{n}'(\boldsymbol{\varepsilon} - 1)\}^{-1}(1/a^3) \tag{16}$$

A comparison with the expressions for the reaction tensor in anisotropic dielectrics given in previous papers shows that the result in Ref. 8 corresponds to Eq. (15), while those reported in Refs. 5 and 9 are incorrect.

It is interesting to note that, while both expressions reduce to the exact formula for the isotropic case, they have a different behavior when the permittivity anisotropy is large.

DISCUSSION

For an anisotropic medium composed of non-polar molecules, a generalized Clausius–Mossotti relation between molecular polarizability and dielectric permittivity can be stated when the field acting on a molecule is known. If the molecule is enclosed in a cavity surrounded by the continuum, the local field is the sum of the cavity and reaction fields:

$$\begin{aligned}\mathbf{F} &= \mathbf{E}_c + \mathbf{E}_r \\ &= \mathbf{g}\mathbf{E}_0 + N^{-1}\mathbf{f}\mathbf{P} \\ &= \{\mathbf{g} + (4\pi N)^{-1}\mathbf{f}(\boldsymbol{\varepsilon} - 1)\}\mathbf{E}_0 \\ &= \{1 + \mathbf{n}(\boldsymbol{\varepsilon} - 1)\}\mathbf{E}_0\end{aligned} \tag{17}$$

N is the number density and the other symbols have already been defined. The last equality has been obtained making use of the expressions for $\mathbf{g}$ Eq. (11) and for $\mathbf{f}$ Eq. (14), and adopting Onsager's hypothesis $VN = 1$. The average value of $\mathbf{F}$ in the laboratory coordinate frame is given by:

$$\langle \mathbf{F} \rangle = \{1 + \langle \mathbf{n} \rangle(\boldsymbol{\varepsilon} - 1)\}\mathbf{E}_0 \tag{18}$$

since only the cavity depolarization tensor $\mathbf{n}$ depends upon the molecu-

lar orientation. For an axially symmetric medium, composed of spheroidal molecules, the components of the average local field are:

$$\langle F_x \rangle = \langle F_y \rangle = \tfrac{1}{3}\{\epsilon_{xx} + 2 + (n_\parallel - n_\perp)S(\epsilon_{xx} - 1)\}E_{0x}$$

$$\langle F_z \rangle = \tfrac{1}{3}\{\epsilon_{zz} + 2 - 2(n_\parallel - n_\perp)S(\epsilon_{zz} - 1)\}E_{0z} \tag{19}$$

where $\epsilon_{xx} = \epsilon_{yy}$ and ϵ_{zz} are the principal components of the permittivity tensor, while $n_\parallel$ and $n_\perp$ are the depolarization factors of the molecular spheroid and the degree of order is defined as usual by $S = \frac{1}{2}(3\cos^2\beta - 1)$.

The Eqs. (19) may be compared with a recent statistical derivation[14] and experimental determination[15] of the internal field in anisotropic fluids. By averaging the molecular dipolar contributions over the two-particle correlation function $g(r, r')$, the following expression for the internal field has been obtained:[14]

$$\mathbf{F}_g = \{\tfrac{1}{3}(\boldsymbol{\varepsilon} + 2) + \boldsymbol{\eta}(\boldsymbol{\varepsilon} - 1)\}\mathbf{E}_0 \tag{20}$$

The anisotropy tensor $\boldsymbol{\eta}$ is traceless and diagonal in the laboratory frame. From refractive index measurements on the nematic phase of EBBA, the principal value η_{zz} is found to be almost linearly dependent upon the degree of order[15]

$$\eta_{zz} \sim 0.16\ \mathrm{S}. \tag{21}$$

The Eqs. (19) give a molecular interpretation of the statistical analysis developed in Ref. 14. By comparison between Eqs. (19) and (20), it follows that:

$$\eta_{zz} = -\tfrac{2}{3}(n_\parallel - n_\perp)S = (\tfrac{1}{3} - n_\parallel)S, \tag{22}$$

and from Eq. (21) we obtain:

$$n_\parallel \sim 0.17; \quad a_\parallel/a_\perp \sim 2.$$

where $a_\parallel$ and $a_\perp$ are the longitudinal and transverse dimensions of the spheroidal cavity.

Finally we note that Eq. (14) should be no longer exact to compute the reaction field in the case of a polar molecule. In fact it is well known that, for a cavity in an isotropic dielectric, the reaction fields of a point dipole or a distributed dipole density are different, unless a spherical cavity is considered.[13] If the cavity has a spheroidal shape, and the point dipole lies along the axis, its reaction field is given by the sum of an infinite series. However the first term of this expansion is just the reaction field of a homogeneous dipole density, while the average of all the other terms vanishes. I feel therefore that Eq. (14) should

give the dominant term of the reaction field tensor for polar molecules in anisotropic as well as in isotropic dielectrics.

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