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Models for ionic contribution to the complex dielectric constant of nematic liquid crystals

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We analyze the models that account the ionic contribution to the complex dielectric constant of a nematic liquid crystal. We compare the predictions of the model of [Sawada *et al.*, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **318**, 225 (1998)] based on the assumption that the electric field in the liquid coincides with the applied one, with the model of Macdonald where the electric field in the sample is determined in self-consistent manner by solving the equation of Poisson. We show that the model of Sawada *et al.*, widely used to determine the bulk density of ions and their diffusion coefficient in liquid crystal cells, predicts a thickness dependence of the real and imaginary parts of the dielectric constant different from that predicted by the model of Macdonald. On the contrary, the predictions of the two models coincide for what concerns the frequency dependencies of the two components of the dielectric constant. By considering a typical case, we show that the numerical values of the ionic properties derived by means of the model of Sawada *et al.* may differ even more than 1 order of magnitude by those predicted by the model of Macdonald. A rescaling procedure allowing to evaluate the bulk density of ions and the ionic diffusion coefficient determined by means of the model of Sawada *et al.* in agreement with the one of Macdonald is proposed.

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I. INTRODUCTION

Nematic liquid crystals are used for the production of displays [1]. These usually contain ions, coming from the aligning layers, chemical decomposition of the molecules forming the liquid crystal itself, or from the decomposition of impurities present in the liquid crystal [2–6]. The presence of the ions in the nematic liquid crystals poses problems for the image quality of the displays. These problems are due to the movement of the ions under the effect of the external field applied to the display to modify its optical properties. The main problems related to the presence of the ions are:

(1) image sticking, due to the persistence of the image, when the external field has been switched off [7];

(2) flicker, which is the modulation of the transmitted light trough a display when the external field has been switched on [8,9];

(3) dependence of the electro-optic characteristic on the frequency and ion concentration [10,11]; and

(4) nonuniformity of the electric field across the display [8].

The equations describing the influence of the ions on the effective dielectric constant of an insulating liquid have been discussed long ago by Macdonald [12], and applied to several situations of practical interest [13–17]. They are the equations of continuity for the positive and negative ions, and the equation of Poisson for the actual potential across the cell. Unfortunately, the final expressions for the real and imaginary parts of the dielectric constant are rather complicated, and their use to interpret experimental data not straightforward. For this reason Sawada *et al.* [18] extended a previous model by Uemura [19,20] to evaluate the influence of the ions on the effective dielectric constant of a nematic liquid crystal by assuming that the actual electric field in the sample coincides with the external one. Our aim is to compare the model proposed by Sawada and co-workers with the one proposed by Macdonald [12]. We will show that the thickness dependencies predicted by the former model for the real, ε_r, and imaginary, ε_i, parts of the dielectric constant of an insulating liquid containing ions are not in agreement with the ones predicted by the latter model. Consequently, the bulk density of ions as well as their diffusion coefficients derived by means of the model of Sawada may differ even more than 1 order of magnitude by those predicted by the model of Macdonald. Our paper is organized as follows. In Sec. II we discuss the model of Sawada *et al.* [18] and obtain the frequency dependencies of ε_r and ε_i in the limit of small and large frequencies of the applied voltage. In Sec. III the same analysis is done in the framework of the model of Macdonald [12]. The comparison of the two models is reported in Sec. IV, where a rescaling procedure allowing to evaluate the bulk density of ions and the ionic diffusion coefficient determined by means of the model of Sawada *et al.* in agreement with those predicted by the model of Macdonald is proposed. The conclusions of the paper are reported in Sec. V, where the thickness dependencies predicted by the two models are discussed. Since the actual electric field across the sample depends on the ionic distribution, which in turn depends on the actual electric field, the assumption over which is based the model of Sawada *et al.* is not realistic. Consequently, since the predictions of the two models differ, the experimental determination of the ionic characteristics in nematic liquid crystals based on the model of Sawada *et al.* are not correct, and have to be used just as a very rough approximation of the true ones.

II. MODEL OF SAWADA *et al.*

Sawada *et al.* [18] assumed that: the ionic recombination can be neglected, the mobilities of the positive and negative

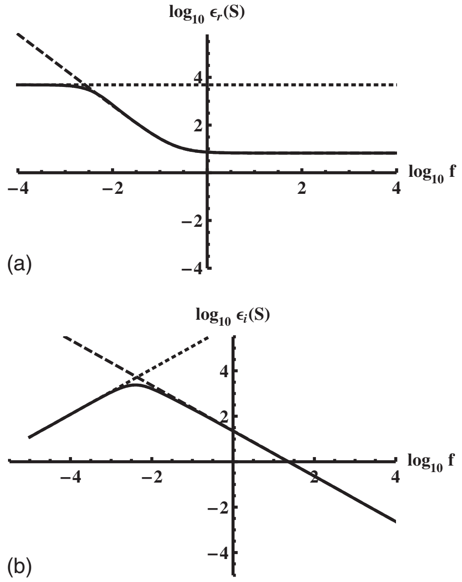

FIG. 1. Frequency dependence of the logarithm of the real (a) and imaginary (b) part of the dielectric constant of an insulating liquid containing ions, according to the model of Sawada *et al.* [18], where the actual electric field in the sample is assumed coinciding with the external one. Dotted lines represent the approximated expressions valid in the dc limit, whereas the dashed lines the approximated expressions in the high-frequency limit.

ions are identical, the electrodes of the sample are perfectly blocking, the actual electric field in the sample coincides with the external one.

In this framework the equations of continuity of the positive and negative ions have been solved, and the electric polarization of ionic origin evaluated. Using the expression for the electric polarization so determined the real, $\varepsilon_r(S)$, and imaginary, $\varepsilon_i(S)$, parts of the effective dielectric constant have been calculated, where S indicate that we are considering the model of Sawada *et al.* [18]. In the analysis of Sawada *et al.* the sample is supposed in the shape of a slab of thickness d and surface area Σ. We indicate by: ε_b the dielectric constant of the liquid free of ions, N the bulk density of the positive and negative ions, in thermodynamical equilibrium, D their diffusion coefficient, q the modulus of their electrical charge, ε_0 the dielectric constant of the vacuum, K_BT the thermal agitation energy, $\omega = 2\pi f$ the angular frequency of the external voltage applied to the sample. With these symbols the expressions for $\varepsilon_r(S)$ and $\varepsilon_i(S)$ in the model proposed by Sawada *et al.* [18] are

$$\varepsilon_r(S) = \varepsilon_b - B\frac{1 + 2e^A \sin A - e^{2A}}{1 + 2e^A \cos A + e^{2A}},$$

$$\varepsilon_i(S) = AB\left\{1 + \frac{1 - 2e^A \sin A - e^{-2A}}{A[1 + 2e^A \cos A + e^{2A}]}\right\}, \tag{1}$$

where

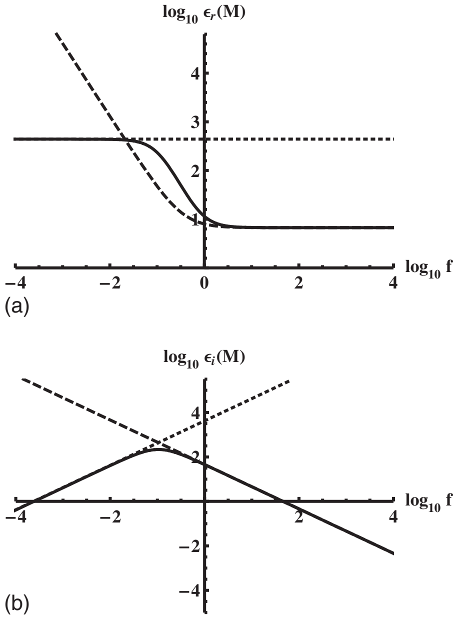

FIG. 2. Frequency dependence of the logarithm of the real (a) and imaginary (b) part of the dielectric constant of an insulating liquid containing ions, according to the model where the actual electric field in the sample is evaluated by solving the equation of Poisson relating the actual potential to the excess of ionic charge. Dotted lines represent the approximated expressions valid in the dc limit, whereas the dashed lines the approximated expressions in the high-frequency limit.

$$A = d\sqrt{\frac{\omega}{2D}}, \quad \text{and} \quad B = \frac{Nq^2}{2\varepsilon_0 K_B T d}\left(\frac{2D}{\omega}\right)^{3/2}. \tag{2}$$

Equation (1) has been used to characterize the ions dissolved in nematic liquid crystals by Sawada *et al.*, mainly to determine their bulk densities in thermodynamical equilibrium, and diffusion coefficients [21–25]. From Eq. (1) we get that in the limit of $\omega \to 0$ the real and imaginary parts of the effective dielectric constant tend to

$$\varepsilon_r(S) = \varepsilon_b\left\{1 + \frac{1}{6}\left(\frac{d}{2\lambda}\right)^2\right\} + \mathcal{O}(\omega^2),$$

$$\varepsilon_i(S) = \frac{1}{60}\varepsilon_b\left(\frac{d}{2\lambda}\right)^2\frac{\omega d^2}{D} + \mathcal{O}(\omega^{5/2}), \tag{3}$$

where we have introduced the length of Debye defined by [26]

$$\lambda = \sqrt{\frac{\varepsilon_b K_B T}{2Nq^2}}. \tag{4}$$

From expression (3), in the case of $\lambda \ll d$, it follows that in the dc limit $\varepsilon_r(S)$ tends to a constant value, proportional to $(d/\lambda)^2$, and $\varepsilon_i(S)$ tends to zero as ω and is proportional to d^4.

In the opposite limit where $\omega \to \infty$ from Eq. (1) one obtains the approximated expressions

$$\varepsilon_r(S) = \varepsilon_b\left\{1 + \frac{2}{d\lambda^2}\left(\frac{D}{2\omega}\right)^{3/2}\right\},$$

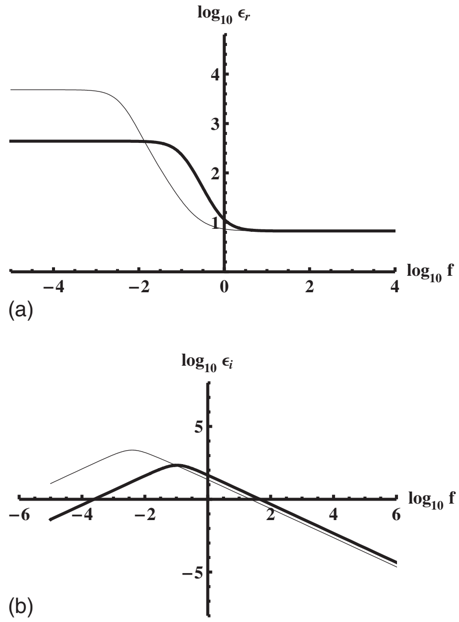

FIG. 3. Comparison of the logarithm of the real (a) and imaginary (b) parts of the dielectric constant obtained by means of the Sawada's model (thin continuous lines) with Macdonald's model (thick lines). The disagreement between the two models is rather large, in particular in the dc limit.

$$\varepsilon_i(S) = \frac{D}{2\omega\lambda^2}\varepsilon_b. \tag{5}$$

From Eqs. (5) we get that in the high-frequency limit, the ions do not contribute to the effective dielectric constant of the insulating liquid in which they are dispersed, as expected. In particular, $\varepsilon_r(S) \to \varepsilon_b$ as $\omega^{-3/2}$, and $\varepsilon_i(S) \to 0$ as ω^{-1}.

III. MODEL OF MACDONALD

We have recently considered the same problem of the renormalization of the dielectric constant of a dielectric liquid containing ions [27], following the line proposed by Macdonald long ago [12], where the actual potential across the sample is evaluated in a self-consistent manner by solving the equation of Poisson. By assuming that the recombination of the ions can be neglected, the electrodes are perfectly blocking, the diffusion coefficients for the positive and negative ions are identical, and the external voltage is so small that the fundamental equations of the problem can be linearized [28], we have shown that the electrical impedance, Z, of a cell in the shape of a slab of thickness d and surface area Σ is given by [27]

$$Z = -i\frac{2}{\omega\varepsilon_b\beta^2\Sigma}\left\{\frac{1}{\lambda^2\beta}\tanh\left(\frac{\beta d}{2}\right) + i\frac{\omega d}{2D}\right\}, \tag{6}$$

where

$$\beta = \frac{1}{\lambda}\sqrt{1 + i\frac{\omega}{D}\lambda^2}. \tag{7}$$

The analysis reported in [27] has been generalized to the case in which the diffusion coefficient of the positive ions differs from the one of the negative ions [29,30], or to the case in which several groups of ions are dispersed in the insulating liquid [31]. The results reported in [27,29,30] confirm the results obtained long time ago by Macdonald in [14,17] that were unknown to the authors of the present manuscript in 2005.

From Eq. (7) a simple calculation allows the determination of the real, R, and imaginary X, parts of Z. The equivalent conductivity, σ_{eq}, and dielectric constant, $\varepsilon_{\mathrm{eq}}$, of the liquid containing ions, defined by the relations

$$\sigma_{\mathrm{eq}} = \frac{1}{R}\frac{d}{\Sigma}, \quad \text{and} \quad \varepsilon_{\mathrm{eq}} = -\frac{1}{\omega X}\frac{d}{\Sigma}, \tag{8}$$

can also be easily evaluated. By introducing the complex dielectric constant $\epsilon = \varepsilon_r - i\varepsilon_i$, and the complex capacitance $\mathcal{C} = \epsilon(\Sigma/d)$, related to the electrical impedance of the cell by the relation $Z = 1/(i\omega\mathcal{C})$, we obtain that [27]

$$\varepsilon_r(M) = \frac{\varepsilon_{\mathrm{eq}}}{1 + \omega^2(\varepsilon_{\mathrm{eq}}/\sigma_{\mathrm{eq}})^2},$$

$$\varepsilon_i(M) = \frac{\omega(\varepsilon_{\mathrm{eq}}/\sigma_{\mathrm{eq}})}{1 + \omega^2(\varepsilon_{\mathrm{eq}}/\sigma_{\mathrm{eq}})^2}\varepsilon_{\mathrm{eq}}, \tag{9}$$

where M indicates that we are working in Macdonald's model. As shown in [27], in the limit of $\omega \to 0$ from Eq. (9) we get,

$$\varepsilon_r(M) = \varepsilon_b\frac{d}{2\lambda}\coth\left(\frac{d}{2\lambda}\right) + \mathcal{O}(\omega^2),$$

$$\varepsilon_i(M) = \frac{1}{8}\varepsilon_b\frac{d}{D}\left\{-d - 6\lambda\coth\left(\frac{d}{2\lambda}\right) + 3d\coth\left(\frac{d}{2\lambda}\right)^2\right\} + \mathcal{O}(\omega^{5/2}), \tag{10}$$

that in the case where $\lambda \ll d$ can be rewritten as

$$\varepsilon_r(M) = \varepsilon_b\frac{d}{2\lambda}, \quad \text{and} \quad \varepsilon_i(M) = \frac{1}{4}\varepsilon_b\frac{d^2}{D}\omega. \tag{11}$$

It follows that in the dc limit $\varepsilon_r(M) \propto d$ and $\varepsilon_i(M) \propto d^2$. In the opposite limit where $\omega \to \infty$ from Eq. (9) we obtain the approximate expressions [27]

$$\varepsilon_r(M) = \varepsilon_b\left\{1 + \frac{4}{d\lambda^2}\left(\frac{D}{2\omega}\right)^{3/2}\right\},$$

$$\varepsilon_i(M) = \frac{D}{\omega\lambda^2}\varepsilon_b. \tag{12}$$

Approximate expressions (11) and (12) strongly differ from the ones deduced by the model of Sawada *et al.* [Eqs. (3) and (5)].

IV. COMPARISON OF THE TWO MODELS

For the numerical calculation we assume that the medium in which are dispersed the ions is the nematic liquid crystal 5CB, and that the limiting surfaces of the sample are treated

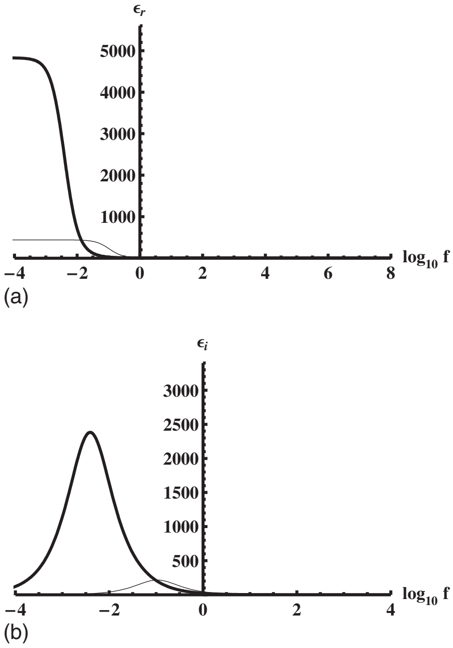

FIG. 4. Comparison of the real (a) and imaginary (b) parts of the dielectric constant obtained by means of the Sawada model's (thin continuous lines) with Macdonald's model (thick lines).

in such a manner to induce planar alignment of the nematic director. In this case, in the considered limit of small applied external voltage, $\varepsilon_b = 6.7\times\varepsilon_0$. We assume furthermore $D = 10^{-12}$ m^2/s, $N = 20\times 10^{19}$ m^{-3}, and that the ions are monovalent with $q = 1.6\times 10^{-19}$ A·s [21,22]. The geometrical parameters of the cell are assumed $d = 20\times 10^{-6}$ m and $\Sigma = 10^{-4}$ m^2, as in typical nematic displays.

In Figs. 1 and 2 we show the frequency dependencies of $\log_{10}\varepsilon_r(S)$ and $\log_{10}\varepsilon_i(S)$ given by Eq. (1), and $\log_{10}\varepsilon_r(M)$ with $\log_{10}\varepsilon_i(M)$ obtained by Eq. (9), respectively. In the same figures we show also approximated expressions (3), (5), (11), and (12), respectively. As it follows from the quoted figures, the agreement between complete expressions and approximated expressions is rather good in a large frequency range.

In Fig. 3 we compare $\log_{10}\varepsilon_r(S)$ with (a) $\log_{10}\varepsilon_r(M)$ and $\log_{10}\varepsilon_i(S)$ with (b) $\log_{10}\varepsilon_i(M)$, and in Fig. 4 we compare $\varepsilon_r(S)$ with $\varepsilon_r(M)$ (a), and $\varepsilon_i(S)$ with (b) $\varepsilon_i(M)$. From Figs. 3 and 4 it is evident that the formulas obtained with the model of Sawada *et al.* strongly differ from the ones obtained by taking into account that the actual electric field in the sample differs from the external one. In particular, for $\omega\to 0$, $\varepsilon_r(S)\propto(d/2\lambda)^2$, whereas $\varepsilon_r(M)\propto(d/2\lambda)$. In the same limit the imaginary parts of the dielectric constant tend to 0 as ω, but $\varepsilon_i(S)\propto d^4$, and $\varepsilon_i(M)\propto d^2$.

In the opposite limit of $\omega\to\infty$, the real parts differ for the quantity

$$\varepsilon_r(S) - \varepsilon_r(M) = -2\frac{\varepsilon_b}{d\lambda^2}\left(\frac{D}{2\omega}\right)^{3/2}, \tag{13}$$

that tends to zero in the considered limit. In the same limit the imaginary parts tend to zero as ω^{-1}, and $\varepsilon_i(S) = \varepsilon_i(M)/2$.

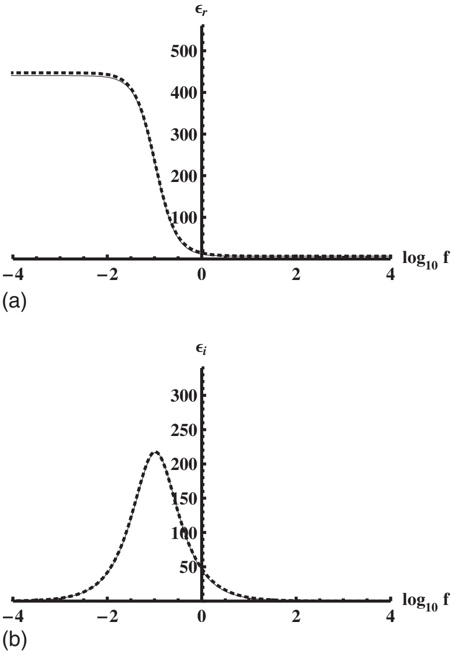

FIG. 5. Comparison of the real (a) and imaginary (b) parts of the dielectric constant obtained by means of the Sawada model's (thin continuous lines) with Macdonald's model (dotted lines), when the bulk density of ions and the diffusion coefficients of the ions have been rescaled as discussed in the text.

From the analysis reported above it is possible to evaluate the difference between the predictions of the model of Sawada *et al.* [18] with respect to the one of Macdonald [12] on the parameters of interest, N and D. For a nematic cell the thickness, d, and the surface area of the electrodes, Σ, are known quantities, as well as the dielectric constant at 1 KHz, ε_b, where the influence of the ions is negligible. We indicate by N_S and D_S the parameters entering in the model of Sawada *et al.*, and by N and D those entering in the model of Macdonald. In the framework where the length of Debye is very small with respect to the thickness of the sample the approximate expressions for the real and imaginary parts of the dielectric constant are given by Eqs. (3), (5), (11), and (12). By imposing that in the limit of $\omega\to 0$, $\varepsilon_r(S)$ and $\varepsilon_i(S)$ coincide with $\varepsilon_r(M)$ and $\varepsilon_i(M)$, given by Eqs. (3) and (11), we get

$$\lambda_S^2 = \frac{1}{12}\lambda d, \quad \text{and} \quad D_S = \frac{1}{5}\frac{d}{\lambda}D, \tag{14}$$

where λ_S is the length of Debye related to the bulk density of ions N_S determined by means of the model of Sawada *et al.* On the other hand, by imposing that the imaginary parts predicted by the two models coincide in the limit $\omega\to\infty$, we obtain

$$D_S = \frac{1}{6}\frac{d}{\lambda}D. \tag{15}$$

It follows that, to have agreement between the two models the effective diffusion coefficient is between (1/5) and (1/6) of $(d/\lambda)D$, and the Debye length λ_S is, as it follows from Eq.

(14), a kind of geometrical average between the thickness of the sample and the actual length of Debye. When $\lambda \ll d$ the values determined by means of the model of Sawada *et al.* can be orders of magnitude different from those predicted by the model of Macdonald. In Fig. 5 we compare the predictions of the model of Sawada *et al.* with those of the model of Macdonald, using the rescaling procedure described above. With our numerical values, using Eqs. (14) and (15) we get $N_S \sim 1.8 \times 10^{19}$ m^{-3} and $D_S \sim 2.6 \times 10^{-11}$ m^2/s. The agreement is rather good, but $N/N_S \sim 10$ and $D/D_S \sim 0.025$.

As a consequence of the possibility of rescaling discussed above, and taking into account that the model of Sawada *et al.* [18] predicts for the real and imaginary parts of the dielectric constant the frequency dependencies coincident with the ones predicted by the model of Macdonald, it is not surprising that a good agreement has been observed between the model of Sawada *et al.* and the experimental data reported in [18,21–25], and more recently in [32,33].

We observe that from the approximate expressions for ε_i, Eqs. (11) and (12), it follows that the angular frequency separating the low from the high-frequency range is $\omega_B = 2D/(\lambda d)$, in agreement with the result reported by Bazant *et al.* [34]. The angular frequency ω_B defines the position of the maximum of $\log_{10} \varepsilon_i$ versus $\log_{10}(\omega/2\pi)$, as it is evident from Fig. 2. This result does not follow from the approximate expressions obtained in the framework of the model of Sawada *et al.* [Eqs. (3) and (5)]. From these equations it follows that the angular frequency separating the low from the high-frequency range is $\omega^* = \sqrt{120}D/d^2$, i.e., of the order of the diffusion frequency, independent of the bulk density of ions.

V. CONCLUSION

From the analysis reported above it follows that the model proposed by Sawada *et al.*, where the electric field in the liquid crystal is assumed equal to the external one, is not in agreement with the model of Macdonald, where the electric field in the liquid crystal is evaluated in a self-consistent manner by solving the equation of Poisson. The experimental determination of the ionic properties deduced by means of the Sawada's model may differ even more than 1 order of magnitude by the ones predicted by the model of Macdonald. A rescaling procedure allowing to evaluate the correct bulk density of ions and the ionic diffusion coefficient determined by means of the model of Sawada *et al.* has been proposed. Nevertheless, according to us, the more realistic model is the one proposed by Macdonald because it considers the actual electric field in the sample by taking into account the equation of Poisson.

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