Calculation of the dielectric constant of monolayers with dielectric anisotropy

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Abstract

The dielectric constant of a monolayer with dielectric anisotropy on a material surface is calculated, assuming that a two-dimensional array is formed and the orientational distribution of rod-like molecules is ruled by Boltzmann statistics. The theoretical local electric field acting on dipoles is taken into consideration in this calculation. It is found that at the molecule density where the maximum tilt angle is $\theta_A = \theta_k = \sqrt{3} - 1)/2$, i.e. $A/A_0 = \sqrt{3}/2$ ($A_0 = \pi l^2$, l is the length of the long axis of rod-like molecule), the dielectric anisotropic monolayer films degenerate to dielectric-isotropic films with an apparent electronic polarizability $\bar{\alpha} = (\alpha_{||} + \alpha_{\perp})/2$, regardless of molecular configuration. Under the mean-field approximation the biaxial molecules degenerate to uniaxial ones with an apparent dipole moment $\mu \cos\theta_D$ and the dependence of dielectric constant on g (see Eq. (9)) is found to be linear. © 1998 Elsevier Science S.A. All rights reserved

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1. Introduction

The dielectric constant of insoluble monolayers has been analyzed for several decades. One of the most important results was the calculation of the local electric field of a hexagonal closed-packing uniaxial dipole array on a water surface reported by Topping [1]. The calculation of dielectric constant of monolayers is often carried out using mean-field theory, in which dipole–dipole interaction should be considered. The calculation of the dipole–dipole interaction can be simplified by introducing a parameter, like the interaction constant g reflecting the in-plane molecular configuration as reported in Refs. [2,3]. This study was carried out assuming a priori that a two-dimensional dipole array is formed on a material surface. For some artificial two-dimensional alignments of dipoles, g has been calculated [4]. The dielectric constant of the monolayer depends on the alignment of the array and orientation of the constituent dipoles in the monolayers as well as the density of the dipoles [5,6]. In the present study, taking into account the dielectric anisotropy due to the biaxiality of molecules in organic monolayers, we extend our previous calculation of the dielectric

constant of dielectric isotropic monolayers on a material surface [5] to the case of the dielectric constant of monolayers with dielectric anisotropy. The dependence of dielectric constant on molecular configuration is also discussed.

2. Analysis

The monolayer model used in the present study is illustrated in Fig. 1, which is similar to that used in our previous studies [5,7]. A plane infinite array of identical point dipoles is located on a material surface with a relative dielectric constant ϵ_m, where each molecule occupies a mean molecular area A on the surface. The molecular dipole with a moment μ is assumed in the long molecular axis at the distance σl with $0 < \sigma < 1$ from the terminal point at the material surface. The effect of biaxiality [8] is taken into consideration by introducing an angle θ_D of the dipole from the long molecular axis. The distribution of the tilted angle θ, the angle between the molecular long axis and the normal direction to the material surface, i.e. the z direction of the laboratory frame, is governed by the intermolecular interaction and the interaction of the dipole with the substrate. The dipoles are assumed to be restricted within the angular range (θ, θ_A), with $\theta_A = \sqrt{A/A_0}$. In order to examine the effect of biaxiality, we consider a frame fixed in a molecule

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with Euler angles $(\varphi, \theta, \gamma)$ defined as the convention in Ref. [9]. In the molecular frame, the z direction is expressed as $z/z = (\sin\theta\sin\gamma, -\sin\theta\cos\gamma, \cos\theta)$. Let the Euler angle of dipole moment be $\mu/\mu = (\sin\theta_D, 0, \cos\theta_D)$ in the molecular frame, we then have the relation:

$$\cos\theta_L = (z/z) \cdot (\mu/\mu) = \sin\theta\sin\gamma\sin\theta_D + \cos\theta\cos\theta_D \qquad (1)$$

Because of the cyclic symmetry of the dipole array, the orientational distribution obeys Boltzmann statistics. In a manner similar to that described in our previous paper [10], here we introduce the orientational order parameter which is defined as:

$$S = \int_0^{2\pi} d\gamma \int_0^{\theta_A} \cos\theta_L \frac{\exp\left[-W(\theta, \theta_L)/kT\right]}{Z} \sin\theta d\theta \qquad (2)$$

where k is the Boltzmann constant, T is the temperature, and $W(\theta, \theta_L)$ is the interaction energy. Z is the single-particle partition function written as:

$$Z = \int_0^{2\pi} d\gamma \int_0^{\theta_A} \exp\left[\frac{-W(\theta, \theta_L)}{kT}\right] \sin\theta d\theta \qquad (3)$$

A special case when the interaction energy $W(\theta, \theta_L) = 0$, leads to:

$$S = S_0 = \frac{\cos\theta_D(1 + \cos\theta_A)}{2} \qquad (4)$$

The addition of $\cos\theta_D$ to the definition of S_0 in Ref. [7] is due to the orientational deviation of the dipole moment μ from the long molecular axis. In other words, the deviation creates an apparent dipole moment $\mu \cos\theta_D$ along the long molecular axis [10].

The relative dielectric constant ϵ of monolayers represents the degree of depolarization. As the depolarization of monolayer is, in fact, reflected by the average dipole moment m_z of the depolarized moment m, it can be defined as [5]:

$$\epsilon = \frac{m_{z0}}{m_z} = \frac{\mu S_0}{m_z} \qquad (5)$$

where m_{z0} and m_z are the average dipole moments of the monolayer before and after depolarization. It is very important to calculate the average dipole moment m_z of the monolayer before and after depolarization. The state of the monolayer before depolarization corresponds to the situation when no interaction is working among the constituent rod-like dipoles.

As has been pointed out by many investigators [2,3], the constituent dipoles depolarize from a dipole moment μ for a single isolated dipole to a value m due to the electric field E_0 produced by the infinite dipole array on a material surface. The average dipole moment m_z of a depolarized dipole m is given by:

$$m_z = \mu S + 4\pi\epsilon_0 E_0 \langle \overset{\leftrightarrow}{\alpha} \cdot n \cdot n \rangle \qquad (6)$$

where S is the orientational order parameter in the case of $W(\theta, \theta_L) \neq 0$, n is the normal direction of the material sur-

face expressed as $(0, \cos\theta, \sin\theta)$, E_0 is the local field produced by neighboring dipoles, and $\overset{\leftrightarrow}{\alpha}$ is the electronic polarizability tensor for the single dipole, which is a rotational ellipsoid in the Cartesian coordinate fixed in the concerned molecule, with the z'-axis along the long molecular axis (see Fig. 1). $\overset{\leftrightarrow}{\alpha}$ is written as (Eq. (7)):

$$\overset{\leftrightarrow}{\alpha} = \begin{pmatrix} \alpha_\perp & 0 & 0 \\ 0 & \alpha_\perp & 0 \\ 0 & 0 & \alpha_\parallel \end{pmatrix} \qquad (7)$$

Here $\alpha_\parallel$ and $\alpha_\perp$ are the electronic polarizabilities along and perpendicular to the long molecular axis of a single molecule, respectively.

Substituting the matrix of $\overset{\leftrightarrow}{\alpha}$ above and the vector of normal direction n into Eq. (6), we obtain:

$$m_z = \mu\langle\cos\theta_L\rangle + 4\pi\epsilon_0 \bar{\alpha} E_0 \left(1 + \frac{\Delta\alpha}{2\bar{\alpha}}\langle\cos 2\theta\rangle\right) \qquad (8)$$

where $\overset{\leftrightarrow}{\alpha} = (\alpha_\parallel + \alpha_\perp)/2$ and $\Delta\alpha = \alpha_\parallel - \alpha_\perp$. Eq. (8) has an additional average dipole moment induced by the effect of dielectric anisotropy $\Delta\alpha$. The biaxiality of molecules is also taken into consideration in $\langle\cos\theta_L\rangle$ in Eq. (8). For $\Delta\alpha = 0$ and $\theta_D = 0$, i.e. $\alpha_\parallel = \alpha_\perp$ and $\theta_D = 0$, Eq. (8) returns to the case of isotropy, as discussed in our previous paper [5].

The depolarization field E_0 at the origin in Eq. (8) is produced by the origin-excluded infinite array of dipoles.
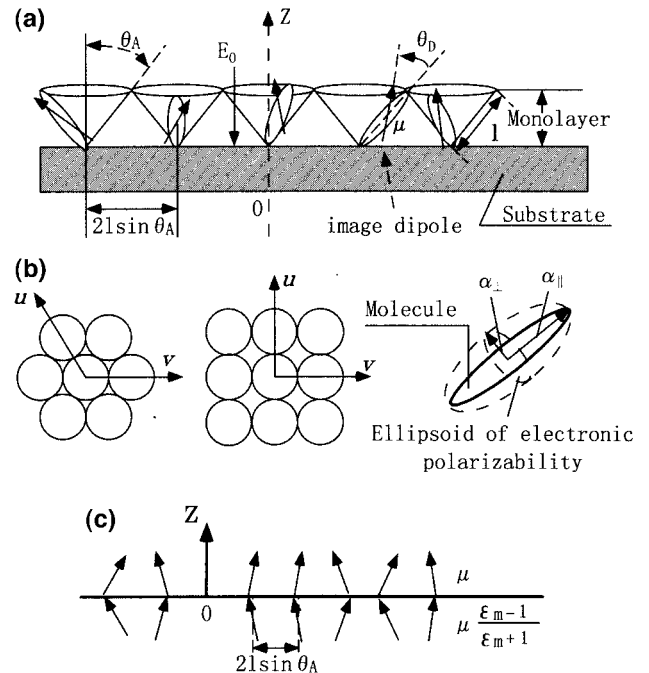

Fig. 1. (a) Model of an infinite array of dipoles on a material surface and the image dipoles for the calculation of the molecule-surface interaction. Rod-like molecules are orientationally distributed, and the dipoles tilt with an angle θ_D from the molecular long axis. (b) The top-view of the infinite array of dipoles in the cases of hexagonal packing and square packing. (c) Image dipoles for the calculation of the local field E_0 at the origin.

The electric field created by a single-point dipole, with a moment m along the z-direction in the plane $z = 0$, is given by [11]:

$$E_0 = -\frac{m_z}{4\pi\epsilon_0} \cdot \frac{2\epsilon_m}{\epsilon_m + 1} \cdot \sum_{dipoles} r_i^{-3} \equiv -\frac{gm_zA^{-3/2}}{2\pi\epsilon_0} \qquad (9)$$

where r_i is the in-plane distance of the molecules from the origin, ϵ_m is the relative dielectric constant of the material surface, for example, the water surface $\epsilon_m = 80$, and g is a parameter reflecting the molecular configuration of monolayers given by:

$$g = A^{3/2} \sum_{dipoles} r_i^{-3} \qquad (10)$$

As ϵ_m is usually much greater than 1, we let $2\epsilon_m/(\epsilon_m + 1) \approx 2$. With Eq. (5), Eq. (8) and Eq. (9), we obtain:

$$\epsilon = \frac{S_0}{S}\left[1 + 2g\bar{\alpha}A^{-3/2} + gA^{-3/2}\Delta\alpha\langle\cos 2\theta\rangle\right] \qquad (11)$$

Eq. (11) gives the generalized relative dielectric constant ϵ of monolayers with consideration of the orientational distribution of dipoles, the effect of the interaction of the substrates, and the dielectric anisotropy of molecules. The biaxiality of molecules is also considered in the definition of orientational order parameter ($S = \langle\cos\theta_L\rangle$). The depolarization effect is included in the orientational order parameter S and the second term, whereas the dielectric anisotropy of molecules is included in the third term in Eq. (11).

3. Discussion

With Eq. (1), (2), (3) and (4), the thermal average $\langle\cos 2\theta\rangle$ can be calculated as:

$$\langle\cos 2\theta\rangle \approx \frac{1}{3}(2\cos^2\theta_A + 2\cos\theta_A - 1) \qquad (12)$$

It is interesting to find from Eq. (11) and Eq. (12) that in the case of $2\cos^2\theta_A + 2\cos\theta_A - 1 = 0$, i.e. (Eq. (13))

$$\cos\theta_A \equiv \cos\theta_k = \frac{\sqrt{3} - 1}{2} \qquad (13)$$

the effect of the dielectric anisotropy due to the geometrical average vanish, under the assumption that second-order coupling between the orientational distribution of molecules and the dielectric anisotropy is negligibly small. This case corresponds to $A/A_0 = \sin^2\theta_A = \sqrt{3}/2$. The dielectric anisotropic monolayer degenerates to a dielectric isotropic one with an apparent electronic polarizability $\bar{\alpha} = (\alpha_\parallel + \alpha_\perp)/2$.

Under the mean-field theory, it is possible to express imtermolecular interaction as:

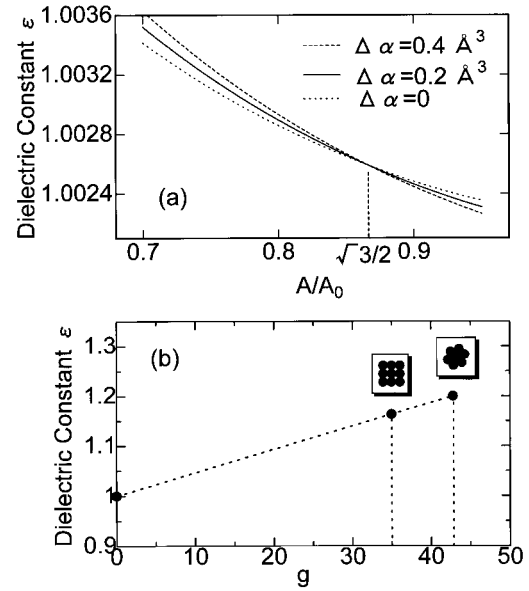$$W(\theta, \theta_L) = -\mu E_0\cos\theta_L \qquad (14)$$

Fig. 2. (a) Simulation result of the relative dielectric constant of a monolayer film on a material surface under the mean-field approximation. Dashed lines ($\Delta\alpha = 0.2\text{Å}^3$) and broken lines($\Delta\alpha = 0.4$ Å^3) correspond to the results of the present calculation, with a consideration of the dielectric anisotropy. Dotted lines ($\Delta\alpha = 0$) are based on the dielectric isotropic approximation. (b) The dependence of relative dielectric constant on the g parameter reflecting the molecular configuration at the molecular area $A/A_0 = 0.05$ with $\Delta\alpha = 0.4$ Å^3. We choose two artificial packings, hexagonal packing ($g = 42.77$) and square packing ($g = 34.99$), as examples.

With Eqs. (1), (2) and (3), we get the approximate orientational order parameter S:

$$S = S_0 + \frac{(1 - \cos\theta_A)^2\cos^2\theta_D}{12}\frac{\mu E_0}{kT} \qquad (15)$$

With Eqs. (8), (9), (11), (14) and (15), we obtain the relative dielectric constant for monolayers with dielectric anisotropy:

$$\epsilon = 1 + 2g\alpha A^{-3/2} + \frac{\mu^2\cos^2\theta_D(1 - \cos\theta_A)^2}{24\pi\epsilon_0 kT}gA^{-3/2} +$$

$$gA^{-3/2}\Delta\alpha\langle\cos 2\theta\rangle \qquad (16)$$

Eq. (16) gives the relative dielectric constant under the mean-field approximation. The first two terms are the results obtained by Macdonald and Barlow [2], and the third term corresponds to the orientational effect of constituent molecules, which is given in our previous paper [5]. It is found from Eq. (16) that the biaxial molecules degenerate to uniaxial ones with an apparent dipole moment $\mu\cos\theta_D$, under the mean-field approximation. Fig. 2a shows the simulation result in the case of hexagonal packing, which is the configuration of maximum nearest-neighbor separation distance and hence of minimum electrostatic interaction energy for any given packing. Monolayers with dielectric anisotropy degenerate to dielectric isotropic ones at the molecular area $A = \sqrt{3}A_0/2$. We choose two artificial packings, the square packing and the hexagonal packing as examples in Fig. 2b, to show the linear relation between

dielectric constant and the g parameter reflecting the molecular configuration. Fig. 2b reveals that the closest-packing hexagonal molecular configuration has the largest dielectric constant compared with other molecular configurations.

4. Conclusion

The dielectric constant of dielectric anisotropic monolayer films is calculated. It is found that when the maximum tilt angle $\theta_A = \theta_k = (\sqrt{3} - 1)/2$, i.e. $A/A_0 = \sqrt{3}/2$, the dielectric anisotropic monolayer films degenerates to dielectric isotropic ones, regardless of molecular configuration. Under the mean-field approximation the biaxial molecules degenerate to uniaxial ones with an apparent dipole moment $\mu\cos\theta_D$ and the dependence of relative dielectric constant on g is found to be linear.

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