

## Analysis of dielectric relaxation time of organic monolayer films on a material surface

Mitsumasa Iwamoto and Chen-Xu Wu

Department of Physical Electronics, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152, Japan

(Received 21 November 1996; revised manuscript received 30 April 1997)

Based on the Debye theory of rotational Brownian motion, we derived the dielectric relaxation time  $\tau$  of monolayers on a material surface in a generalized form.  $\tau$  was found to be proportional to the orientational fluctuation of monolayers [ $=\langle(\cos\theta-\langle\cos\theta\rangle)^2\rangle$ ] ( $\theta$  is the tilt angle of the constituent polar molecules). Here  $\langle\cos\theta\rangle$  represents the molecular orientational order parameter of monolayers, and  $\langle\rangle$  represents the thermal average. In this analysis, the Coulomb attractive force working between polar molecules and the material surface as well as the interaction working among molecules were taken into consideration. It was revealed that the interaction working on molecules makes a significant contribution to reduce the relaxation time whether the interaction is attractive or repulsive. [S1063-651X(97)04809-5]

PACS number(s): 68.15.+e, 31.70.Hq, 82.20.Rp

Dielectric relaxation phenomena in dielectric materials, including organic materials, lipids, and liquids have been a subject of many studies in various fields: physics, chemistry, electronics, biology, etc. Debye studied the rotational Brownian motion of molecules with permanent electric dipoles in liquids, and developed a method for the analysis of the dielectric relaxation phenomena [1]. Since then, many studies of the dielectric bulk materials have been carried out on the basis of the Debye philosophy [2–4]. Recently, these studies were applied to an analysis of the dielectric relaxation phenomena in organic monolayer and multilayer films, assuming *a priori* that the dielectric behavior of polar molecules in monolayer and multilayer films is the same as that of polar molecules in bulk materials [5]. However, this assumption is not suitable for a profound understanding of the dielectric behavior of polar molecules in monolayer films. The constituent molecules of monolayer films deposited by, for example, the Langmuir-Blodgett technique, align on a material surface, and as-deposited films have spontaneous polarization in the absence of an external electric field. The Coulomb attractive force working between polar molecules and the material surface directly effects the polar orientational alignment of polar molecules. Further, the molecular motion of rodlike molecules on a material surface is spatially restricted in the region of the hemisphere, owing to the presence of the material surface. Thus it is important to develop a generalized theory for the analysis of dielectric relaxation phenomena in organic monolayers on a material surface.

In our previous study [6], starting from the Debye Brownian motion equation [7], we derived an equation representing the transient behavior of the orientational order parameter  $S$  of polar molecules on a material surface. We then analyzed the transient dielectric behavior of monolayers on a water surface under lateral monolayer compression by means of the Maxwell-displacement-current-measuring technique. In that analysis, we obtained the dielectric relaxation time  $\tau$  of monolayers as functions of viscosity constant, temperature, and the tilt angle of polar molecules away from normal direction to the water surface, under the assumption that the effect of the attractive force working between polar molecules and the water surface, as well as the interaction working among the constituent polar molecules, can be ignored.

However, this analysis was not sufficient for a profound understanding of the dielectric relaxation phenomena in organic monolayers on a material surface, possibly because these interactions directly effect the motion of polar molecules. In this Brief Report, we derive the dielectric relaxation time of monolayers on a material surface in a generalized form, taking into account these aforementioned interactions.

The model of monolayer used in the present paper is shown in Fig. 1(a). Briefly, the monolayer consists of rodlike polar molecules with a length  $l$ . Each molecule has a permanent dipole moment  $\mu$  in the direction along its long axis, and it stands on a material surface (electrode 2) at a tilt angle  $\theta$  away from the normal direction to the material surface. The monolayer film is sandwiched between electrodes 1 and 2, which are separated at a distance  $L$  by an air gap. All of the molecules can align on electrode 2 when the molecular area  $A < A_0 (= \pi l^2)$ . The orientational distribution of the constituent molecules of the monolayer film is ruled by

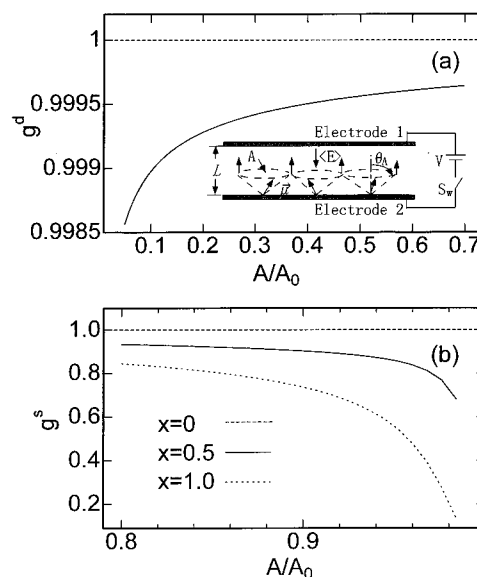


FIG. 1. Interaction coefficient  $g$  with respect to the relative molecular area  $A/A_0$ . (a)  $g^d$  in the region with a small molecular area, and (b)  $g^s$  in the region with a molecular area close to  $A_0$ .

Boltzmann statistics, and its motion is expressed by the rotational Debye Brownian motion equation [7]

$$\frac{\partial \omega(\theta, t)}{\partial t} = \frac{1}{\xi \sin \theta} \frac{\partial}{\partial \theta} \left[ \sin \theta \left( kT \frac{\partial \omega(\theta, t)}{\partial \theta} + \frac{\partial W(\theta, t)}{\partial \theta} \omega(\theta, t) \right) \right], \quad (1)$$

where  $\omega(\theta, t)$  is the possibility function representing the possibility of the molecules standing on a material surface at time  $t$ ,  $\xi$  is the friction constant of monolayer, and  $W(\theta, t)$  is the interaction energy working on molecules.  $W(\theta, t)$  contains the dipole-surface interaction  $W_s(\theta)$ , dipole-dipole interaction  $W_d(\theta)$ , and the additional interaction  $W_{\text{ex}}(\theta, t)$  produced by external stimulations such as the electric field. The first term on the right-hand side of Eq. (1) represents the possibility flow due to the thermal motion of the environment obeying the law of Fick. The second term is the flow due to the effect of internal interaction working among molecules and the interaction produced by the application of an external stimulation. We assume here that the motion of rod-like polar molecules is restricted within  $0 < \theta < \theta_A$ , where  $\theta_A = \sin^{-1} \sqrt{A/A_0}$ , principally due to effects of hard core intermolecular forces. The possibility function  $\omega(\theta, t)$  satisfies the following relation at the equilibrium state, which is given by [6]

$$\omega(\theta, 0) \sim \exp \left\{ -\frac{W_{\text{int}}(\theta)}{kT} \right\}. \quad (2)$$

Here  $W_{\text{int}}(\theta)$  is the sum of the molecule-molecule interaction  $W_d(\theta)$  and the molecule-surface interaction  $W_s(\theta)$ . In our previous studies, we used Eq. (2) for a calculation of the dielectric constant of monolayers [8], thermally stimulated discharge current across monolayers [9], and Maxwell displacement current (MDC)  $I_{\text{eq}}$  generated by monolayer compression [10].

The orientational order parameter of monolayers on a material surface is defined as [10]

$$S = \int_0^{\theta_A} \cos \theta \omega(\theta, t) \sin \theta \, d\theta. \quad (3)$$

With Eqs. (1) and (3), we find that  $S$  satisfies the following equation [6]:

$$\frac{\partial S}{\partial t} = \int_0^{\theta_A} \frac{1}{\xi} \sin^2 \theta \left( kT \frac{\partial \omega(\theta, t)}{\partial \theta} + \frac{\partial W(\theta, t)}{\partial \theta} \omega(\theta, t) \right) d\theta. \quad (4)$$

In order to examine the dielectric relaxation phenomena in monolayers, we assume here that a step additional interaction force  $RU(t)$  ( $U(t)$  is a unit step function) is applied to monolayers in the direction perpendicular to the material surface by the application of a step external stimulation. All molecules on a material surface experience an additional interaction in a same way. In this case,  $W(\theta, t)$  is given by

$$W(\theta, t) = W_{\text{int}}(\theta) - RU(t) \cos \theta. \quad (5)$$

$-RU(t) \cos \theta$  is the interaction produced by the external stimulation.

As aforementioned,  $-RU(t) \cos \theta$  is considered as a perturbation working to the equilibrium state, and influences the orientational distribution of dipoles slightly. Therefore Eq. (4) is rewritten as [6]

$$\begin{aligned} \frac{\partial S}{\partial t} &= \frac{RU(t)}{\xi} \int_0^{\theta_A} \sin^2 \theta \omega(\theta, t) \sin \theta \, d\theta \\ &\approx \frac{RU(t)}{\xi} (1 - \langle \cos^2 \theta \rangle), \end{aligned} \quad (6)$$

where  $\langle \cos^2 \theta \rangle$  is the thermal average due to the interaction  $W_{\text{int}}$  at  $t=0$ . In addition to the term given in Eq. (6), the total rate of change of  $S$  contains a term due to thermal relaxation motion. The thermal motion will tend to restore the orientational distribution of molecules to the equilibrium distribution in the absence of external stimulation. Introducing  $1/\tau$  as a proportionality factor, the total rate of change of  $S$  is written as

$$\frac{d(S - S_{\text{eq}})}{dt} = -\frac{S - S_{\text{eq}}}{\tau} + \frac{1 - \langle \cos^2 \theta \rangle}{\xi} RU(t), \quad (7)$$

where  $\tau$  is the dielectric relaxation time, and  $S_{\text{eq}}$  is the order parameter at the equilibrium state before the application of the external stimulation. Here  $S_{\text{eq}}$  is the orientational order parameter at  $t=0$ , whose distribution is ruled by Eq. (2). Equation (7) describes the transient behavior of a monolayer, that is, the dielectric relaxation phenomena in monolayers by the application of the external stimulation. The monolayer experiences an additional interaction  $-R \cos \theta$  soon after the application of an external stimulation, and the total interaction is expressed as Eq. (5). In the equilibrium state at time  $t=\infty$ , the orientational distribution of polar molecules can be expressed by Boltzmann distribution function again and is given by

$$\begin{aligned} \omega(\theta, \infty) &= \frac{\exp\{-W(\theta)/kT\}}{Z}, \\ &= \frac{\exp[-W_{\text{int}}(\theta)/kT]}{Z} \left\{ 1 + \frac{R \cos \theta}{kT} \right\}, \end{aligned} \quad (8)$$

under the assumption  $|R/kT| \ll 1$ . Here the partition function  $Z$  is expressible as

$$Z = Z_0 + \frac{R}{kT} S_{\text{eq}} Z_0, \quad (9)$$

where  $Z_0$  is the single-partition function at  $t=0$ . From Eqs. (8) and (9), we obtain the orientational order parameter  $S$  at time  $t=\infty$  as follows:

$$\begin{aligned} S &= \int_0^{\theta_A} \cos \theta \omega(\theta, \infty) \sin \theta \, d\theta \\ &= S_{\text{eq}} - \frac{R}{kT} (\langle \cos \theta \rangle^2 - \langle \cos^2 \theta \rangle), \end{aligned} \quad (10)$$

where  $\langle \cos \theta \rangle$  and  $\langle \cos^2 \theta \rangle$  are the thermal averages before external stimulation. At the equilibrium state at  $t = \infty$ , the relation  $d(S - S_{\text{eq}}^e)/dt = 0$  is satisfied. Therefore, from Eqs. (7) and (10), we obtain the dielectric relaxation time

$$\tau = \frac{\xi}{kT} \frac{\langle (\cos \theta - \langle \cos \theta \rangle)^2 \rangle}{1 - \langle \cos^2 \theta \rangle}. \quad (11)$$

Equation (11) gives the dielectric relaxation time  $\tau$  in a generalized form, which is proportional to the orientational fluctuation of monolayers  $\langle (\cos \theta - \langle \cos \theta \rangle)^2 \rangle$ , and is inversely proportional to the diffusion coefficient ( $= kT/\xi$ ) [7]. The denominator  $(1 - \langle \cos^2 \theta \rangle)$  is related to direction of the external stimulation [see Eq. (7)].

In order to calculate the dielectric relaxation time  $\tau$  given by Eq. (11), we need to calculate the  $\langle \cos \theta \rangle (= S_{\text{eq}})$  and  $\langle \cos^2 \theta \rangle$  in advance. The mean-field approximation is applicable to the case of monolayers with a small molecular area  $A$  ( $A < A_0$ ). In this region, the monolayer is governed by the molecule-molecule interaction  $W_d$ .  $W_d$  is written as [8]

$$W_d = \frac{11.0342 \mu m_z}{4 \pi \epsilon_0 a^3} \frac{2 \epsilon_m}{\epsilon_m + 1} \cos \theta, \quad (12)$$

under the assumption of the uniform and hexagonal molecular packing, which is the configuration of nearest-neighbor separation distance and hence of the minimum electrostatic interaction energy for any given packing. Here  $\epsilon_m$  is the relative dielectric constant of monolayer supporting materials,  $a$  is the nearest molecular separation distance between adjacent two molecules, and  $m_z$  is the average polarized dipole moment of monolayers, which is given by

$$m_z = \frac{\mu S_0}{(1 + 11.0342 a^{-3} \alpha) [2 \epsilon_m / (\epsilon_m + 1)]}, \quad (13)$$

where  $\alpha$  is the electronic polarizability of molecules.  $S_0$  is the orientational order parameter  $[= (1 + \cos \theta_A)/2]$  in the zero interaction. With Eqs. (2) and (3), the orientational order parameter  $S_{\text{eq}}^d (= \langle \cos \theta \rangle)$  and  $\langle \cos^2 \theta \rangle$  under these interactions are calculated as

$$\begin{aligned} \langle \cos \theta \rangle &= S_0 + \frac{\eta_d}{12} (1 - \cos \theta_A)^2 \\ \langle \cos^2 \theta \rangle &= \frac{1}{3} (1 + \cos \theta_A + \cos^2 \theta_A) + \frac{\eta_d S_0}{6} (1 - \cos \theta_A)^2, \end{aligned} \quad (14)$$

where  $\eta_d$  is expressed as

$$\eta_d = - \frac{11.0342 \mu m_z}{4 \pi \epsilon_0 k T a^3} \frac{2 \epsilon_m}{\epsilon_m + 1}.$$

Here  $\epsilon_0$  is the dielectric constant of a vacuum. Substituting Eq. (14) into Eq. (11), we obtain

$$\tau^d = g^d \tau_0 = \left[ 1 + \frac{\eta_d S_0 (1 - \cos \theta_A)}{2(2 + \cos \theta_A)} \right] \frac{\xi}{4kT} \frac{1 - \cos \theta_A}{2 + \cos \theta_A}. \quad (15)$$

Here  $g^d$  given by

$$g^d(\theta_A) = 1 + \frac{\eta_d S_0 (1 - \cos \theta_A)}{2(2 + \cos \theta_A)} \quad (16)$$

is an interaction coefficient representing the effect of molecule-molecule interaction.  $\tau_0$  ( $= (\xi/4kT)[(1 - \cos \theta_A)/(2 + \cos \theta_A)]$ ) is the relaxation time obtained under the condition that both molecule-molecule interaction and molecule-surface interaction are ignored, as discussed in our previous paper [6].

In the case of monolayers with the molecular area  $A$  close to the critical area  $A_0$ , the interaction between molecules and the material surface become much important in comparison with the molecule-molecule interaction. This interaction is given by [11]

$$W_s(\theta) = - \frac{\mu^2}{16 \pi \epsilon_0 \epsilon_m l^3 \cos \theta} \frac{\epsilon_m - 1}{\epsilon_m + 1}. \quad (17)$$

The dielectric relaxation time is mainly affected owing to the presence of the interface. The orientational order parameter  $S_{\text{eq}} (= \langle \cos \theta \rangle)$  and  $\langle \cos^2 \theta \rangle$  can also be calculated by substituting Eq. (17) into Eqs. (2) and (3) [10],

$$\begin{aligned} \langle \cos \theta \rangle &= \frac{x}{2} + \frac{e^x - \cos^2 \theta_A e^{x/\cos \theta_A}}{2[e^x - \cos \theta_A e^{x/\cos \theta_A} + x\{\text{Ei}(x/\cos \theta_A) - \text{Ei}(x)\}]} \\ &\quad \times \langle \cos^2 \theta \rangle \\ &= \frac{1}{3} \left\{ \langle \cos \theta \rangle x + \frac{(2\langle \cos \theta \rangle - x)(e^x - \cos^2 \theta_A e^{x/\cos \theta_A})}{e^x - \cos^2 \theta_A e^{x/\cos \theta_A}} \right\}, \end{aligned} \quad (18)$$

where

$$x = \frac{\mu^2}{16 \pi \epsilon_0 \epsilon_m l^3 k T} \frac{\epsilon_m - 1}{\epsilon_m + 1}.$$

The coefficient  $g$  in this case becomes

$$g^s(\theta_A) = \frac{4(2 + \cos \theta_A)}{1 - \cos \theta_A} \frac{\langle \cos^2 \theta \rangle - \langle \cos \theta \rangle^2}{1 - \langle \cos^2 \theta \rangle}, \quad (19)$$

which can be written as

$$g^s(\theta_A) = \frac{P(\theta_A)}{Q(\theta_A)}, \quad (20)$$

with the approximation  $|x| \ll 1$ . Here

$$\begin{aligned} P(\theta_A) &= 1 + x \left\{ - \frac{6(1 + \cos \theta_A)}{(1 - \cos \theta_A)^2} \right. \\ &\quad \left. - \frac{4(1 + \cos \theta_A + \cos^2 \theta_A)}{(1 - \cos \theta_A)^2} \ln \cos \theta_A \right\} \\ &\quad + x^2 \left\{ - \frac{12}{(1 - \cos \theta_A)^2} - \frac{6(1 + \cos \theta_A)}{(1 - \cos \theta_A)^3} \ln \cos \theta_A \right\} \end{aligned}$$

$$Q(\theta_A) = 1 + x \left\{ -\frac{3}{2} \frac{1 - \cos^2 \theta_A}{2(2 + \cos \theta_A)(1 - \cos \theta_A)^2} + \frac{\cos^2 \theta_A + \cos \theta_A - 5}{(2 + \cos \theta_A)(1 - \cos \theta_A)^2} \ln \cos \theta_A \right\} + x^2 \left\{ -\frac{12}{(1 - \cos \theta_A)^2} + \frac{6(1 + \cos \theta_A)}{(1 - \cos \theta_A)^3} \ln \cos \theta_A \right\}.$$

Figure 1 shows the interaction coefficient  $g$  in the molecular interaction region [ $g^d$  in Fig. 1(a)] and in the region dominated by the molecule-surface interaction [ $g^s$  in Fig. 1(b)]. In Fig. 1(a), we assume  $l=2$  nm,  $T=300$  K,  $\mu=0.7$  D, and  $\alpha=0.65$  Å<sup>3</sup>, as examples. These values were chosen on the basis of Ref. [8]. Figure 1 was plotted in two extreme cases, that is,  $W(\theta) \approx W_d(\theta)$  and  $W(\theta) \approx W_s(\theta)$ .  $g$  is less than 1 in both regions, which reveals that the dielectric relaxation time  $\tau$  becomes shorter due to the molecule-molecule interaction and molecule-surface interaction. The interaction working on molecules, whether it is a repulsive molecule-molecule one or an attractive molecule-surface one, brings a monolayer to a more stable system promptly. As a result the dielectric relaxation time  $\tau$  decreases. The dielectric relaxation time increases as the molecular area increases in Fig. 1(a). This is because in the small molecular area region, the molecule-molecule interaction decreases as the molecular area increases. We may expect that at the molecular area  $A_i = A_0 \sin \theta_i$ , where the repulsive interactive force changes into an attractive one,  $g=1$ , because  $W(\theta_i) = W_d(\theta_i) + W_s(\theta_i) = 0$  at the molecular area  $A = A_i$ . In contrast, in the region  $A > A_i$ , as the molecular area increases, the dielectric relaxation time  $\tau$  decreases because of the increase in the attractive molecule-surface interaction.

From the definition of  $g$ , we may also rewrite the dielectric relaxation in another form,

$$\tau = \frac{\xi'}{4kT} \frac{1 - \cos \theta_A}{2 + \cos \theta_A}, \quad (21)$$

with an apparent viscosity constant  $\xi' = g\xi$ . As  $g < 1$ , the monolayer becomes less viscous as a result of the molecule-molecule interaction and the effect of surface.

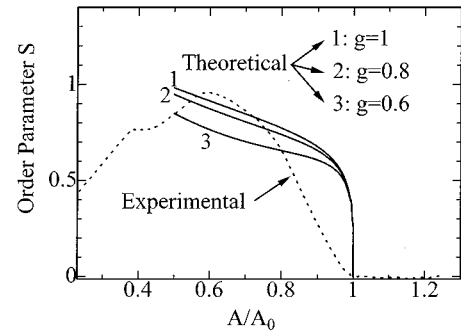


FIG. 2. Experimental order parameter  $S$  and the theoretical  $g$  dependence of the order parameter.

Based on the aforementioned discussion, we reexamined the result of the MDC flowing across 4-cyano-4'-5-alkyl-biphenyl (5 CB) monolayers with monolayer compression, which we reported in our previous paper [see Fig. 3(a) in Ref. [6]]. In Fig. 2, the results were again plotted using the order parameter  $S$ . The interaction coefficient  $g$  depends on the molecular area  $A$ , as shown in Fig. 1. However, for simplicity, here we calculated the order parameter  $S$  using Eqs. (22) and (26) in Ref. [6], replacing  $\xi \rightarrow g\xi$  under the assumption that  $g$  is constant. This simplification does not lose the physics here, because the change in  $g$  is gentle with respect to  $A$  (see Fig. 1). Here it is essential to clarify the effect of the interaction coefficient  $g$ . As seen in Fig. 2, it is found that the order parameter saturates more slowly as the interaction increases, i.e., as  $g$  deviates from 1. This tendency is favorable for explaining the experimental dielectric relaxation phenomena, though there is still a discrepancy between the theoretical curve and the experimental result at the molecular area close to  $A = A_0$ , which may be due to the ignorance of the size effect of the constituent molecules at the molecular area close to  $A_0$  in our model [12] and due to the ignorance of the dependence on  $A$  of  $g$ . The modification of the present model is required, and this is our future task. Nevertheless, the generalized relaxation time given by Eq. (11) is still correct, and it will be helpful for a profound understanding of the dielectric relaxation phenomena in monolayers on a material surface, as well as the frictional property of monolayers on a material surface [2,13].

[1] P. Debye, *Polar Molecules* (Dover, New York, 1929).  
 [2] H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, New York, 1958).  
 [3] R. Chen and Y. Kirsh, *Analysis to Thermally Stimulated Process* (Pergamon, Oxford, 1981).  
 [4] J. van Turnhout, *Thermally Stimulated Discharge of Polymer Electrets* (Elsevier, New York, 1975).  
 [5] J. Tanguy and P. Hesto, *Thin Solid Films* **21**, 129 (1974).  
 [6] M. Iwamoto and C. X. Wu, *Phys. Rev. E* **54**, 6603 (1996).  
 [7] J. McConnell, *Rotational Brownian Motion and Dielectric Theory* (Academic, New York, 1980).

[8] M. Iwamoto, Y. Mizutani, and A. Sugimura, *Phys. Rev. B* **54**, 8186 (1996).  
 [9] M. Iwamoto, C. X. Wu, and W. Y. Kim, *Phys. Rev. B* **54**, 8191 (1996).  
 [10] A. Sugimura, M. Iwamoto, and Z. Ou-Yang, *Phys. Rev. E* **50**, 614 (1994).  
 [11] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York 1976).  
 [12] M. Jiang, F. Zhong, D. Y. Xing, Z. D. Wang, and J. Dong, *J. Chem. Phys.* **106**, 6171 (1997).  
 [13] G. L. Gaines, *Insoluble Monolayers at Liquid-Gas Interfaces* (Science, New York, 1965).