

Dielectric behavior of organic monolayers due to orientational phase transition

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Conventionally, there is only one treatment, i.e., the relaxation-time treatment, for thermally stimulated problems. An alternative thermodynamics approach is examined for its feasibility in calculating the thermally stimulated order parameter, dielectric constant, and current (TSC) of monolayers on a material surface. It was found that the two different phases are attributed to the effect of two different kinds of molecular interactions. The theoretical results also demonstrate the phase-transition feature of the experimental TSC and dielectric constant ϵ_s at a critical temperature T_C . [S0163-1829(96)00435-3]

I. INTRODUCTION

Over the past several decades, many experimental techniques and theoretical methods have been developed for a more profound understanding of the properties of various kinds of monolayers and multilayers.¹ On the one hand, thermally stimulated current (TSC) measurement has been used for studying the dielectric depolarization phenomena as well as the disordering degree of constituent polar molecules in multilayer film systems,² in which the Maxwell-displacement current flowing across multilayer films sandwiched between metal electrodes is recorded during heating, and various peaks appearing at characteristic temperatures are attributed to relevant discharge mechanisms relating to the orientational change in polar molecules, detrapping of electron charges, etc. On the other hand, on the basis of Debye philosophy, Tanguy and Hesto studied the polarization effects associated with initial heating of orthphenanthroline multilayers;³ Jones *et al.* investigated the thermally stimulated discharge of alternate-layer Langmuir-Blodgett (LB) film structures;⁴ and Jonscher discussed thermally stimulated depolarization current (TSD) on multilayers on the basis of the so-called "universal law," and developed a theoretical approach to TSD.⁵ There is unfortunately a drawback in TSD theory which is based on classical mean-field theory with a relaxation-time treatment in explaining the critical phenomena of monolayer and multilayer films. Moreover, it is very difficult to obtain reproducibility in the measurement, in particular in the TSC measurement of a one-layer film, principally due to the destruction of the film by the application of the top electrode.⁶ In one of our previous papers,⁷ we developed a displacement current measuring system equipped with a thermal stimulation system, and investigated TSC across arachidic acid monolayers due to the disordering of multilayers using a metal/monolayer/air-gap/metal structure. It is necessary to try the thermodynamics approach rather than TSD to explain the modern critical phenomena which happen in almost every TSC experiment. In this paper, under the framework of classical mean-field theory, we will calculate TSC with a thermodynamics approach on the basis of analyses developed in our previous papers,^{8,9} and then discuss the TSC of phospholipid monolayers due to the disordering of polar orientation of molecules.

II. ANALYSES

Monolayer and multilayer films exhibit various phases,¹ and it is expected that thermally stimulated current depends on the phases. For simplicity, we discuss the TSC generated in monolayers sketched as the model shown in Fig. 1. In the figure, one monolayer with thickness l is deposited on electrode 2, and it consists of rodlike polar molecules with a permanent dipole moment μ in the direction along the long axis of the molecule. The constituent molecules with a length a are orientationally distributed with a tilt angle θ away from the normal direction to the surface of metal electrode. The molecules are assumed to align in the range $0 < \theta < \theta_A$ due to effects of hard-core intermolecular forces, where $\theta_A = \arcsin(\sqrt{A/A_C})$. The surface density of the constituent molecules is given by $n = 1/A$, where A is the area occupied per molecule. A_C is the critical area occupied by a single molecule and defined as πa^2 . Electrode 1 is suspended in air, and connected to electrode 2 through an ammeter. The vertical component of the effective mean dipole moment $\langle m \rangle$ of the constituent molecule can be expressed as¹⁰

$$\langle m \rangle = \mu S + \alpha \langle E_i \rangle. \quad (1)$$

Here S is the orientational order parameter of monolayers defined as $S = \langle \cos \theta \rangle$, where $\langle \rangle$ denotes a thermodynamics average, and α is the electron polarizability of the constituent molecules. $\langle E_i \rangle$ is the mean depolarization electric field applied to the constituent molecule in a direction perpendicular to the monolayer surface from electrode 2 to air and is given by

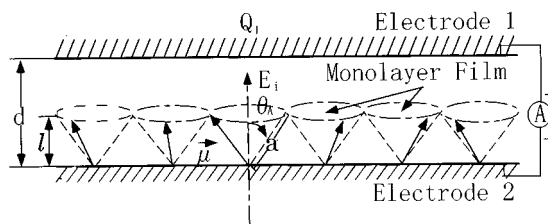


FIG. 1. Sketch of the model for a molecule monolayer at an air-liquid interface.

$$\langle E_i \rangle = \frac{gn\langle m \rangle}{l\epsilon_\infty}, \quad (2)$$

where ϵ_0 is the relative dielectric constant of a vacuum and $g(<0)$ is the interaction constant working on the constituent molecules, and can be calculated depending on the arrangement of the constituent molecules.¹¹ The charge Q_1 is induced on electrode 1 due to the orientational distribution of the constituent polar molecules. Assuming that monolayers are heated at a constant heating rate β , a Maxwell displacement current is generated by the change of the induced charge Q_1 :⁹

$$I = -dQ_1/dt = \frac{\beta nB}{d} \frac{d}{dT} \langle m \rangle, \quad (3)$$

where B is the working area of electrode 1 and d is the distance between electrodes 1 and 2. Using Eqs. (1)–(3), we obtain $\langle m \rangle$ and current I as follows:

$$\langle m \rangle = \frac{\mu S}{\epsilon_\infty} \quad (4)$$

and

$$I = \beta \frac{nB\mu}{d\epsilon_\infty} \frac{dS}{dT}, \quad (5)$$

with $\epsilon_\infty = 1 - \alpha gn/l\epsilon_0$. As described in our previous papers, the dielectric constant ϵ_s of the monolayers is⁹

$$\epsilon_s = \frac{\epsilon_\infty S_0}{S}, \quad (6)$$

where S_0 is the order parameter in the zero field. Substituting Eq. (6) into Eq. (5), we obtain the current:

$$I = \beta \frac{nB}{d} \mu S_0 \frac{d}{dT} \frac{1}{\epsilon_s}. \quad (7)$$

We will calculate S , ϵ_s , and I as functions of temperature T on the basis of the equations above. It is interesting to note here that current I in Y -type multilayer films with odd numbers of layers is given by the same Eqs. (5) and (7), because the permanent dipole moment is canceled out due to the alternating deposition of monolayers with opposite directions layer by layer in the Langmuir-Blodgett technique, and only the contribution of one layer remains as the induced charge on electrode 1.

III. CALCULATION

Because of the axial symmetry, the molecules are considered to be restricted within the range $0 < \theta < \theta_A$ under the mean-field approximation, and the orientational order parameter S is expressed as

$$S = \int_0^{\theta_A} \cos\theta \frac{e^{-W(\theta)/kT}}{Z} \sin\theta d\theta, \quad (8)$$

where Z is the partition function:

$$Z = \int_0^{\theta_A} e^{-W(\theta)/kT} \sin\theta d\theta. \quad (9)$$

Here k is the Boltzmann constant and T the absolute temperature. $W(\theta)$ is the effective self-consistent field due to the interaction of molecules. In a zero field, S becomes

$$S_0 = \frac{1 + \cos\theta_A}{2}. \quad (10)$$

Under the mean-field approximation, constituent rodlike molecules freely rotate in the range of tilt angle $0 < \theta < \theta_A$ under some mean local electric field, and the interaction energy can be written as the form $W = W_0 \cos\theta$. Substituting this into Eq. (8), we obtain

$$S = \frac{e^t - \cos\theta_A e^{t \cos\theta_A}}{e^t - e^{t \cos\theta_A}} \frac{1}{t}, \quad (11)$$

where $t = -W_0/kT$. S is a function which increases monotonously with t . In the limit t is infinity ($t \rightarrow \infty$) S approaches 1, whereas it approaches $S = \cos\theta_A$ in the limit $t \rightarrow -\infty$. Substituting the equation above into Eq. (5), we obtain the general TSC of $W_0 \cos\theta$ -form interaction:

$$I = \beta \frac{nB\mu}{d\epsilon_\infty} \left[-\frac{(1 - \cos\theta_A)^2 e^{t(\cos\theta_A - 1)}}{(1 - e^{t(\cos\theta_A - 1)})^2} + \frac{1}{t^2} \right] \frac{dt}{dT}. \quad (12)$$

We are going to use Eqs. (6), (11), and (12) to discuss the TSC mechanism.

A. In the liquid phase

In the region when $T > T_C$, the intermolecule interaction, which is the main contributor in the highly oriented phase ($T < T_C$), is negligible in the fluid phase compared to the other interactions. Thus under a mean-field approximation the interaction energy can be obtained:

$$W(\theta) = -\mu \langle E_i \rangle \cos\theta. \quad (13)$$

It is instructive here to discuss the case for $|t| < 1$, in which S is written approximately as

$$S = S_0 + \frac{t(1 - \cos\theta_A)^2}{12} = S_0 \left(1 - \frac{A}{T} \right), \quad (14)$$

with $A = -gn\mu^2(1 - \cos\theta_A)^2/12kl\epsilon_0[1 - \alpha(\mu/\epsilon_0)l]g$. On the other hand, the average dipolemoment $\langle m \rangle$ is given approximately by

$$\langle m \rangle = \frac{\mu S_0}{\epsilon_s}, \quad (15)$$

using Eqs. (4) and (6). Here ϵ_s is the relative dielectric constant of the monolayer written as

$$\epsilon_s = \epsilon_\infty \left(1 + \frac{A}{T} \right). \quad (16)$$

Therefore, substituting Eqs. (15) and (16) into Eqs. (3) and (5), the TSC current I is obtained:

$$I = K(T+A)^{-2}, \quad (17)$$

with $K = \beta A \mu S_0 nB/d\epsilon_\infty$. We plotted S , ϵ_s , and I by solid lines as a function of T in Fig. 2. As we can see in the figure, in the region $T > T_C$ the order parameter S gradually in-

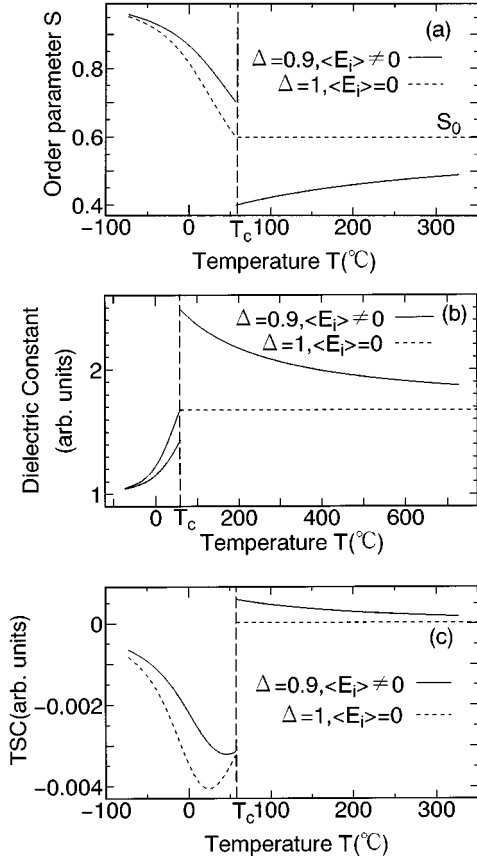


FIG. 2. Theoretical simulation. Dotted lines, with $\Delta=1$, $\cos \theta_A=0.2$, $T_C=330$ K, and $V_0=20kT_C$ for $\langle E_i \rangle=0$. Thin lines, with $\Delta=0.9$, $\cos \theta_A=0.2$, $T_C=330$ K, and $V_0=20kT_C$ for $\langle E_i \rangle \neq 0$. (a) Thermally stimulated order parameter S . (b) Temperature-dependent dielectric constant ϵ . (c) TSC.

creases and approaches S_0 as the temperature increases, whereas the dielectric constant $\epsilon_S - \epsilon_\infty$ decreases. Current I flows in the positive direction—that is, in the direction from electrode 1 to electrode 2 through an ammeter (see Fig. 1)—and gradually decreases. It is instructive here to note that a linear relationship between $\epsilon_S - \epsilon_\infty$ and $1/T$ represents the characteristics of normal dielectric materials.¹⁰ Further, it is interesting to calculate S , ϵ_S , and I in the case $\langle E_i \rangle$, which is reliable when electrode 1 is in contact with monolayers on electrode 2.¹² The results are plotted by dotted lines in Fig. 2. As we can see in the figure, $S=S_0$ and $I=0$ in the region $T>T_C$. Judging from Fig. 2, we may conclude that the internal electric field $\langle E_i \rangle$ works to suppress the polar orientational ordering; that is, the field works to decrease S , whereas the increase in temperature tends to overcome the suppression.

B. In the liquid-crystalline phase

In the liquid-crystalline phase when $T<T_C$, interdipole attractive forces such as the Keesom interaction, which is inversely proportional to temperature T , and other temperature-independent interactions are working among the constituent molecules.¹³ As a result, in such a case of the so-called liquid phase, when the temperature is relatively high, interaction among molecules is small compared with

interaction between molecules and the interface, and in the liquid-crystalline phase, molecules are highly oriented, and interaction among molecules is the dominant factor and should be considered. In the region $T<T_C$, for one molecule, because of the system's space-inversion symmetry, we postulate the interaction as a mean field effect, and the Keesom-form interaction is temperature dependent:

$$W(\theta, T) = -V_0 \left(\frac{T_C}{T} - \Delta \right) \cos \theta - \mu \langle E_i \rangle \cos \theta. \quad (18)$$

Here V_0 is the magnitude of the interaction, Δ the transition order, and $\langle E_i \rangle$ the mean field which is expressible as fS ($f = gn\mu/l\epsilon_0\epsilon_\infty < 0$) according to Eqs. (2) and (4). Thus t is

$$t = \frac{V(T) + \mu \langle E_i \rangle}{kT} = \frac{V_0}{kT} \left(\frac{T_C}{T} - \Delta + \frac{\mu f}{V_0} S \right). \quad (19)$$

In case $|V_0| \gg kT \gg |\mu f|$, i.e., the mean-field effect is negligible, considering Eq. (19) and Eqs. (6), (11), and (12), and we obtain S , ϵ_S and the TSC of region $T<T_C$:

$$S = \frac{1 - \cos \theta_A e^{(\cos \theta_A - 1)(V_0/kT)[(T_C/T) - \Delta]}}{1 - e^{(\cos \theta_A - 1)(V_0/kT)[(T_C/T) - \Delta]}} - \frac{1}{\frac{V_0}{kT} \left(\frac{T_C}{T} - \Delta \right)}, \quad (20)$$

$$\epsilon_S = \frac{\epsilon_\infty S_0}{S} \quad (21)$$

$$I = \beta \frac{nB\mu}{d\epsilon_\infty} \left[- \frac{(1 - \cos \theta_A)^2 e^{(V_0/kT)[(T_C/T) - \Delta](\cos \theta_A - 1)}}{(1 - e^{(V_0/kT)[(T_C/T) - \Delta](\cos \theta_A - 1)})^2} + \frac{1}{\frac{V_0}{kT} \left(\frac{T_C}{T} - \Delta \right)} \right] \left(- \frac{2V_0 T_C}{kT^2} + \frac{\Delta V_0}{kT} \right). \quad (22)$$

It is easy to estimate that, at room temperature, the relation $|\mu f| \ll kT$ is satisfied for the real monolayer film systems, e.g., L - α -dimyristoyl, phosphatidylcholine (DMPC) films, as will be discussed in Sec. V A. Equations (20), (21), and (22) are depicted in Fig. 2. As we can see in the figure, S decreases as the temperature increases, possibly because the intermolecular attractive interaction effect is weakened as the temperature increases, whereas ϵ_S increases and current I flows in the negative direction as the temperature increases. It is obvious from Fig. 2 that the transition temperature is easily determined from the Maxwell-displacement current (MDC) measurement, because the direction of current changes at the transition temperature T_C .

While in case $|V_0| \ll |\mu f| \ll kT$, $t = t' + (\mu f/kT)S$. Under a simple approximation, Eq. (11) leads to

$$S = \frac{S(t')}{1 - \left(\frac{\partial S}{\partial t'} \right) \frac{\mu f}{kT}} = S(t') + \left(\frac{\partial S}{\partial t'} \right) S(t') \frac{\mu f}{kT}, \quad (23)$$

where $S(t')$ is expressed as Eq. (11), and

$$t' = \frac{V_0}{kT} \left(\frac{T_C}{T} - \Delta \right).$$

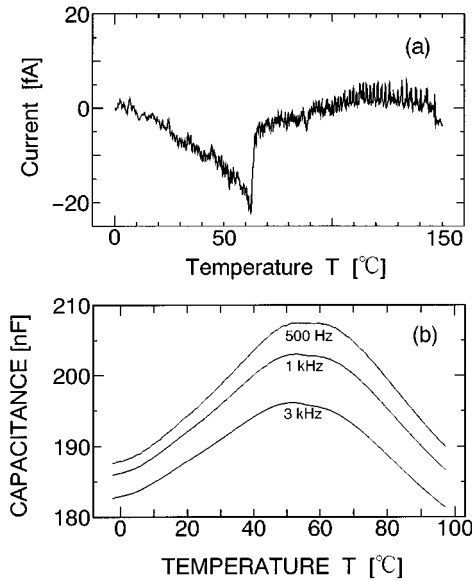


FIG. 3. (a) Experimental TSC of DMPC ($Y-5$, $\beta=0.02$ °C/s). (b) Temperature-dependent capacitance ($Y-3$, $\beta=0.02$ °C/s).

The dielectric constant and Maxwell-displacement current can also be obtained by Eqs. (6) and (7).

IV. EXPERIMENT

The experimental system was the same as in our previous study.⁷ The TSC of a five-layer *L*- α -dimyristoyl, phosphatidylcholine (DMPC) film was measured at a heating rate β of 0.2 °C/s, and plotted in Fig. 3(a). Here the film was prepared with the conventional vertical dipping method in the LB technique at a surface pressure of 30 mN/m by raising and dipping the substrate through an air-water interface. The molecular area ($A = 1/n$) of the deposited DMPC film was about 63 Å². It is found that the direction of current changes abruptly at a temperature of 60 °C, corresponding to the transition temperature,¹³ and that this directional change in current reproducibly appears during heating by cyclic heating and cooling. In order to examine the dielectric behavior of DMPC, the capacitance of three-layer DMPC multilayers sandwiched between aluminium metal electrodes was measured by increasing the temperature as a function of frequency. The results were plotted in Fig. 3(b). The capacitance climbs up to a maximum at 60 °C and then decreases after the transition.¹⁴

V. DISCUSSION

A. Phase transition

The theoretical thermally stimulated current expressed by Eqs. (17) and (22) and plotted in Fig. 2(c) appears to have a shape similar to the experimental result shown in Fig. 3(a), where the direction of current changes at a transition temperature of 60 °C. This result suggests that the mean-field effect is negligibly small, and the relation $|\mu f| \ll kT \ll V_0$ is satisfied in the temperature range between 0 and 60 °C ($=T_C$). In order to clarify this suggestion, here we calculate the value of $\mu f/kT$. From the results of a MDC measurement of DMPC,¹⁵ we may assume that the dipole moment μ is

about 0.65~0.80 D, and the length of the DMPC molecule a is 9.44 Å. Further, as we described in Sec. IV, the molecular density n (1/Å) is estimated to be 1.6×10^{18} m⁻². Thus the value of $\mu f/kT$ is estimated to be about 2.4×10^{-4} for $g=1$, $\epsilon_\infty=1.2$, and $T=300$ K. Therefore we may conclude that the relation $|\mu f| \ll kT \ll V_0$ is satisfied in our experimental results. As we can see from the calculation results plotted in Figs. 2(a) and 2(c), TSC becomes smaller as $\langle E_i \rangle$ decreases. In our experiment, μf is very small in comparison with kT in the temperature range $T > T_C$. As a result, our experimental TSC is very small in the range $T > T_C$ [see Fig. 3(a)], as we expected. We are still not clear about the magnitude V_0 , although the theoretical calculation leads to a small cusp at a temperature lower than T_C , which becomes obscure and shifts to a lower temperature as V_0 decreases. A consideration of the relaxation effect is required for a profound understanding of the transition in the experimental TSC curves.

As for the capacitance, the total capacitance C is expressible as

$$\frac{1}{C} = \frac{1}{C_0} + \frac{1}{C_S}, \quad (24)$$

where C_0 is the capacitance of the native aluminium oxide layer formed on the electrodes, and C_S is the capacitance of the film. Thus from Eq. (21) and the expression above, we can easily obtain the same capacitance appearance as in Fig. 3, because the capacitance of the native aluminium oxidelayers is independent of the temperature in the range employed in the TSC measurement.¹²

B. Thermodynamics approach to monolayers

We have described an alternative model which we expect will be more appropriate for explaining TSC phenomena. The experimental TSC shows a sudden direction change at the transition point, which could be employed to determine the critical transition temperature T_C . The conventional relaxation-time treatment, which is based on nonequilibrium thermostatics, has been studied for a couple of decades; however there are still some difficulties in revealing the phase-transition phenomena of monolayers. The present model reveals that, as temperature increases, the monolayer experiences an ordering liquid-crystalline state and a disordering liquid state. The intermolecular interactions, which are temperature dependent, dominate the TSC generation in the liquid-crystalline state. Δ is an index representing the order of phase transition, i.e.,

$$\begin{cases} 0 < \Delta < 1 & \text{first-order transition} \\ \Delta = 1 & \text{second-order transition.} \end{cases}$$

Criteria for a higher-order phase transition require a further comparison between the intermolecule and molecule-interface interactions, and a consideration of the contribution of the mean internal electric field. Because a determination of transition order needs a further experiment, we set $\Delta \neq 1$ and $\Delta = 1$ in the simulation with and without consideration of internal electric field, respectively, to explain the experimental appearance of the capacitance and TSC. The simulation of TSC reveals that the first-order simulation is closer to the experimental TSC than the second-order one.

VI. CONCLUSION

A model concerning phase transition due to molecular orientational disordering in monolayers was established with a thermodynamical approach. The thermally stimulated current, dielectric constant, and orientational order parameter were calculated, and experimental results on DMPC were discussed based on the model presented here. Monolayers under thermal stimulation experience a phase transition from the liquid-crystalline phase to a liquid phase. The estimation that the mean-field effect is negligible in the liquid-crystalline phase shows that two different kinds of interactions dominate the two phases, respectively. An abrupt change of MDC direction occurred at the critical temperature

due to the sudden change of orientational ordering, though a cusp at a temperature lower than T_c in Fig. 2(c) appeared depending on the magnitude of the Keesom interaction V_0 . The phase transition of DMPC is close to a first-order one. The change of dielectric constant can also be discussed by such a model, so long as the orientational order parameter is obtained. By going to a further consideration of the relaxation effect, though complicated, a smoother TSC curve can be expected. Finally it should be noted that the model discussed above relies upon the assumption that molecules are quick enough to respond as temperature increases. Its chief advantage lies in that it can explain the TSC phenomena without calculating the complicated relaxation time.¹⁶

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