Diffusive motion of molecules in submonolayer liquid films on a solid surface

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The spreading of submonolayer liquid polymer films on a solid surface that consist of molecules with different mobilities was investigated. The molecular conformations of the adsorbed and free molecules were estimated from the dispersive surface energy measurement and the relationship between the diffusion coefficient of the free molecules and the coverage of the adsorbed molecules were obtained from the spreading profile measurement. A free mobile molecule lies flat on the solid surface and an adsorbed molecule lies less flat than a mobile one. The relation between the diffusion coefficient and the coverage can be explained by the percolation model at a small coverage and it can be explained by the reptation model at a large coverage.

I. INTRODUCTION

The spreading of thin liquid films on solid surfaces is a subject of soft matter physics attracting the interest of many researchers in these years [1–4]. Especially, the spreading of molecularly thin films has been intensively studied because it is also important for many industrial applications such as lubricant films on disks in computer magnetic recording technology or photoresist films in microelectronics [5–16,22]. At the microscopic scale, relatively thick films can be treated by hydrodynamics where a main motive force is disjoining pressure gradient. On the contrary, the diffusion coefficient for submonolayer film is independent of the film thickness and it is proportional to the temperature [2–4,8]. This means that thermal fluctuation is more dominant than the disjoining pressure in submonolayer films. In most of the analytical studies on the diffusion of submonolayer films, liquid molecules have been assumed to have the same properties and they diffuse in the same manner. However, in more realistic cases, some molecules physically or chemically adsorb on the substrate, and especially, polar molecules tend to adsorb strongly by chemical interaction such as hydrogen bonding. This adsorption leads to the difference in the mobility between the adsorbed and free molecules. In practical applications such as magnetic recording, the spreading properties of monolayer or submonolayer thick lubricant films are controlled by adjusting the ratio of the numbers of adsorbed and free molecules [11,12]. On the contrary, computer simulations such as molecular dynamics (MD) simulation or Monte Carlo (MC) simulation have been extensively developed and they have been applied to analysis of the diffusion of the polar molecules. Philips *et al.* analyzed the spreading of the submonolayer polar liquids by MC simulation although the molecule was assumed to be a simple sphere [13]. Tani *et al.* also analyzed the spreading of the submonolayer

film by MC simulation, where the difference in the mobility was described as that in activation energy [14,15]. Although the computer simulation is a useful tool for the analysis of the spreading, the physical or chemical parameters such as intermolecular interaction potentials, which determine the accuracy of the simulation, are not always easy to obtain for the actual experimental systems. This makes it difficult to compare the experimental results with simulated ones.

In this study, we aim at establishing a fundamental model, which can be compared with experimental results, for the spreading of submonolayer liquid films that consist of the molecules with different mobilities. The molecular conformations of the adsorbed and free molecules was estimated from the surface energy measurement and the relationship between the diffusion coefficient of the free molecules and the coverage of the adsorbed molecules was investigated. An approximate model for explanation of the experimental results will be presented in another short paper [16]. In this paper, significantly more detail and results are presented and two models, the percolation and reptation models, are investigated for explanation of the experimental results. In addition, the normal diffusive range at a longer time is focused on here.

II. MATERIALS AND METHODS

Magnetic disks with a nitrogenated carbon overcoat and a perfluoropolyether (PFPE) lubricant (Fomblin-ZDOL4000, Solvay Solexis) were used as the sample substrate and liquid because the disk surface was molecularly flat and the interaction between the liquid lubricant and the disk has been intensively clarified. The roughness of the disk surface was measured with an atomic force microscope and the roughness R_a was about 0.4 nm. The molecular structure of the lubricant is given by

$$\text{HO-CH}_2\text{-CF}_2\text{-}[(\text{O-CF}_2\text{-CF}_2)_p\text{-}(\text{O-CF}_2)_q]\text{-O-CF}_2\text{-CH}_2\text{-OH},$$

(1)
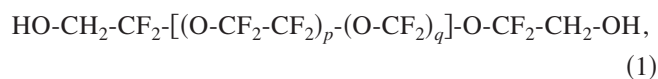
where the ratio p/q is typically between 2/3 and 1. The lubricant, which is widely used in magnetic disk drives, is a

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linear chain polymer having a molecular weight of about 4000 g/mol and the estimated molecular diameter of the gyration is about 3 nm for the bulk and the diameter of the linear chain is about 0.7 nm. The length of the molecule is about 14 nm. The numbers of (OCF_2CF_2) and (OCF_2) groups in a single molecule with a molecular weight of 4000 are 21 and 22 ($p=q=21$). Cotts experimentally obtained the characteristic ratio $C_\infty=5.7$ and the Kuhn statistical segment length $l_K=1.0$ nm for a similar PFPE molecule $(CF_3\text{-}[(O\text{-}CF_2\text{-}CF_2)_p\text{-}(O\text{-}CF_2)_q]\text{-}O\text{-}CF_3, p/q\sim2/3)$ having molecular weights from 2300 to 51300 [17]. From these results, the number of the statistically independent segments is estimated to be about 14 [18].

Using *ab initio* calculation, Waltman *et al.* showed that the molecules adsorbed by the hydrogen bonding between the nitrogen of the overcoat carbon and the hydroxy end groups of the lubricant are thermally stable and the molecules are firmly anchored, while the molecules physically adsorbed by van der Waals force are thermally unstable and easy to move [12]. Here, the molecules anchored by hydrogen bonding are called "bonded" molecules and free or physically adsorbed molecules, which are easy to move, are called "mobile" molecules. The lubricant was applied to sample disks by dip coating. In this method, which is used for the commercial production of hard disk drives, the substrate was immersed and then pulled out of the lubricant solution at a constant speed. The thickness of the liquid film on the substrate could be changed with subnanometer resolution by adjusting the removal speed and the lubricant solution density. The thickness of lubricant films was measured with a commercially available scanning ellipsometer (Five Lab, MARY-102). Annealing the disk coated with lubricants was necessary for generating the bonded molecules. In this process, the hydroxy end group is considered to diffuse to the active bonding sites of the carbon [11]. The bonded molecule films were obtained by rinsing the lubricant-coated disks with a solvent (HFE-7200, 3M) and their thicknesses were adjusted by means of the annealing time. The annealing temperature was set to 130 °C. The thickness measured by the ellipsometer is the sum of the thickness responses from the lubricant-covered and uncovered surfaces of the disk in the laser spot (30×100 μm^2) for submonolayer films. This means that the ellipsometer thickness is proportional to the number of molecules in the laser spot. The bonding ratio b was defined as the ratio of the bonded layer thickness to its maximum thickness and it is considered to be the ratio of the number of the bonding sites occupied by the molecules and total number of the sites.

The dispersive surface energy of the lubricant films γ_{LV}^d was obtained by measuring the contact angle. The contact angle θ of a drop of test liquid on the lubricant-coated disk was measured. In this experiment, *n*-hexadecane was used as the test liquid. The dispersive surface energy γ_{LV}^d was obtained from the contact angle θ as explained below. The surface energy of the interface air/test liquid/lubricant γ_{VTL} is given by [19,20]

$$\gamma_{VTL} = \gamma_{LV} + \gamma_{TV} - 2\sqrt{\gamma_{LV}^d \gamma_{TV}^d}, \tag{2}$$

where γ_{LV} and γ_{TV} are the surface energies of the interfaces air/lubricant and air/test liquid, and subscript d denotes the dispersive components. Using the Young-Dupre's equation, the relation γ_{VTL} and θ can be given by [19,20]

$$\gamma_{VTL} = \gamma_{LV} - \gamma_{TV}\cos\theta. \tag{3}$$

Using Eqs. (2) and (3), we can get the Girifalco-Good-Fowkes-Young's equation,

$$\cos\theta = -1 + \frac{2\sqrt{\gamma_{LV}^d \gamma_{TV}^d}}{\gamma_{TV}} = -1 + 2\sqrt{\frac{\gamma_{LV}^d}{\gamma_{TV}}}. \tag{4}$$

Note that $\gamma_{TV}^d = \gamma_{TV}$ for *n*-hexadecane because it does not have polar surface energy. Because the surface energy γ_{TV} for *n*-hexadecane are known, the dispersive surface energy γ_{LV}^d can be obtained from the measured contact angle θ. In addition, the coverage f of the bonded molecules was obtained by measuring θ and using Cassie-Baxter's law [21],

$$\cos\theta = f\cos\theta_L + (1-f)\cos\theta_C, \tag{5}$$

where θ_L and θ_C are the contact angles of the lubricant and carbon surfaces.

The diffusion coefficient of the mobile molecules moving through the bonded molecules was obtained by the following procedures. Sample disks coated with various coverages of bonded molecules were prepared by rinsing with the solvent after annealing for various times. Using the dip-coating method, additional mobile lubricant films were applied to disks with various coverages of bonded molecules. To create a boundary for the additional lubricant film, the disk was partially immersed in the lubricant-dissolved solvent and then pulled out of the solution at a constant speed. The amounts of additional mobile lubricants were adjusted to be about equal for each sample disk (additional thickness =0.7–0.9 nm). The thickness profile around the boundary $h(x,t)$ was measured with the scanning ellipsometer. Because the diffusion coefficient of the submonolayer film does not depend on the thickness, the boundary profile $h(x,t)$ can be obtained by solving the diffusion equation [5],

$$\frac{\partial h(x,t)}{\partial t} = D\frac{\partial^2 h(x,t)}{\partial x^2}, \tag{6}$$

and the solution of Eq. (6) can be given by

$$h(x,t) = \frac{h_0}{2}\left[1 - \frac{2}{\sqrt{\pi}}\int_0^u e^{-\xi^2}d\xi\right], \tag{7}$$

where h_0 is the initial thickness and $u=x/2\sqrt{Dt}$. The diffusion constant D was obtained by fitting the measured boundary profile to Eq. (7).

III. RESULTS AND DISCUSSION

A. Molecular conformation of mobile and bounded molecules

Figure 1 shows the film thickness dependence of the dispersive surface energies. Figures 1(a) and 1(b) show the dependences of the mobile and bonded molecules. Here, the film without annealing is considered to mainly consist of mobile molecules. In the figures, the dotted lines are the asymptotic limits of the bulk lubricant. The limits were about
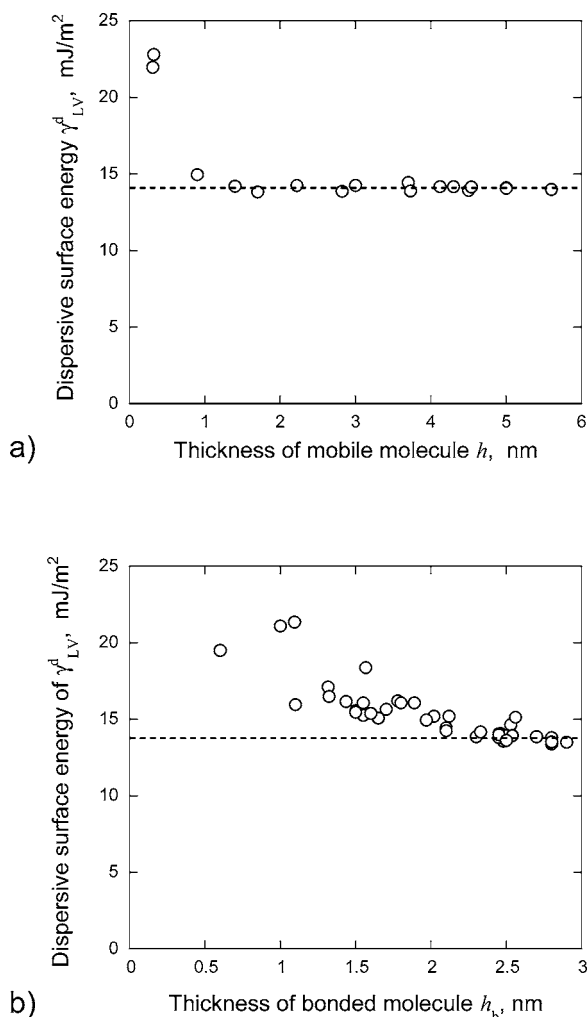
a)

b)

FIG. 1. Film thickness dependence of the dispersive surface energy of (a) mobile molecule and (b) bonded molecule.

1.4 and 2.4 nm for the mobile and bonded molecules, respectively. Tyndall *et al.* reported that the monolayer thickness (the thickness for physically complete coverage) can be determined as the thickness when the dispersive surface energy reaches the asymptotic limit of the bulk lubricant [11]. Using this method, we found that the monolayer thicknesses were about 1.4 and 2.4 nm for the mobile and bonded molecules, respectively. Considering that its molecular diameter in the bulk is about 3 nm, a mobile molecule lies flat on the disk surface and a bonded molecule lies less flat than a mobile one. Mayeed and Kato also reported that the lubricant molecules lie flat on the disk using the MC simulation [22].

Figure 2 shows the relation between the coverage f and bonding ratio b. The bonding ratio b is not proportional to the coverage f. The coverage f is the ratio of the area covered by the bonded molecules, whereas the bonding ratio b is that of the number of the occupied site. Letting A_m, n, A, and N denote the area per one bonded molecule, number of the molecules, total area, and total number of the sites in the whole area, $f=nA_m/A$ and $b=n/N$. Therefore $f/b=A_m/(A/N)$. Letting $A_{mmin}=(A/N)$, A_{mmin} is the area per the bonded molecule when all the bonding sites are occupied ($b=1$). Thus the ratio $f/b=A_m/A_{mmin}$ is the normalized area
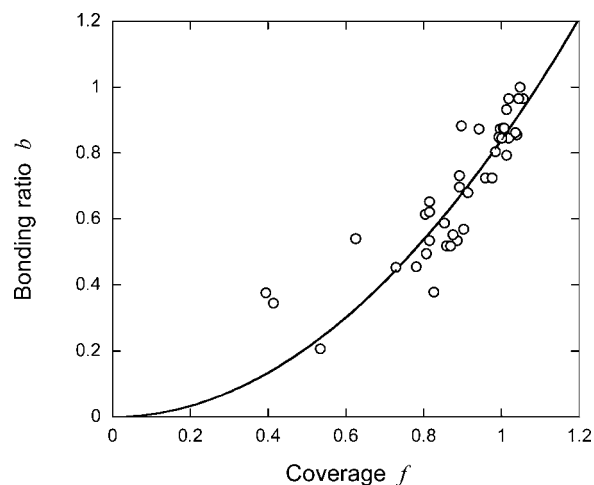

FIG. 2. Measured relationship between the coverage f and bonding ratio b. The solid line is the curve fitting the data to a square function.

covered by one bonded molecule, so, $\sqrt{f/b}$ is proportional to the normalized diameter of one bonded molecule a/a_{min}. Here, a and a_{min} are the diameters when $b<1$ and $b=1$. From the results shown in Fig. 2, the bonding ratio can be approximated by the square function of the coverage f (the solid line in the figure). Therefore $\sqrt{f/b}$ is proportional to $1/\sqrt{f}(a/a_{min}=\beta/\sqrt{f})$. This means that the normalized diameter of one bonded molecule a/a_{min} is proportional to $1/\sqrt{f}$ in this experiment. The area covered by one bonded molecule a/a_{min} is smaller as the coverage f is larger. This may mean that the bonded molecules lie less flat when the coverage f is larger. The decrease in the area covered by one bonded molecule may be due to repulsive interactions between the densely packed molecules.

B. Diffusive motion of mobile molecules

Figure 3 shows the measured spreading profiles around the boundaries for the films with a coverage of 0, 0.38, and 0.91. In the figures, the profiles just after application, after 12 h and after 24 h are shown. Note that the film thickness of added mobile films are shown in these figures. The thicknesses of bonded films are 0, 0.8, and 2.2 nm for the films with a coverage of 0, 0.38, and 0.91, respectively. This result indicates that the mobile molecules that applied to the disk with a higher coverage of the bonded molecules are less fluid. Figure 4 shows the measured relationship between the normalized diffusion coefficient of the mobile molecules and the coverage of the bonded molecules (black circles). The diffusion coefficient was obtained from the spreading profiles after a time long enough, when the diffusion coefficients were almost constant values, and the average values after 20 and 24 h are plotted in the figure. In Fig. 4, D_0 is the diffusion coefficient for the lubricant film without annealing, where most of the molecules on the disk are mobile ones. The higher coverage reduces the diffusion coefficient. This qualitatively agrees with the image that the mobile molecule passes through the bonded ones. The mobile molecules may make their way through a dense forest of bonded ones. Two
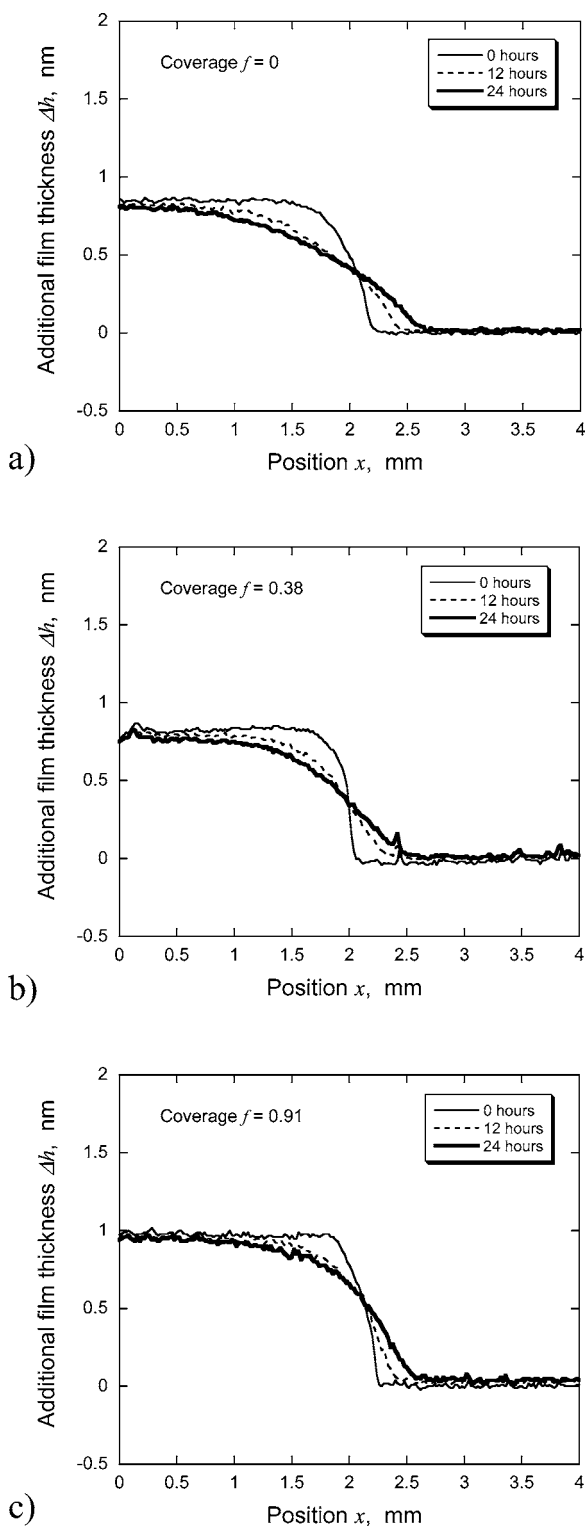
a)

b)

c)

FIG. 3. Measured spreading profiles just after application, and after 12 and 24 h. (a) coverage $f=0$, (b) $f=0.38$, (c) $f=0.91$.

models for the explanation of the experimental results, percolation and reptation models, are discussed below (Fig. 5).

First, the percolation model is discussed. This model can explain the particle diffusion through the frozen background particles with a random distribution as shown in Fig. 5(a) [23]. The mobile and bonded molecules of the liquid lubri-
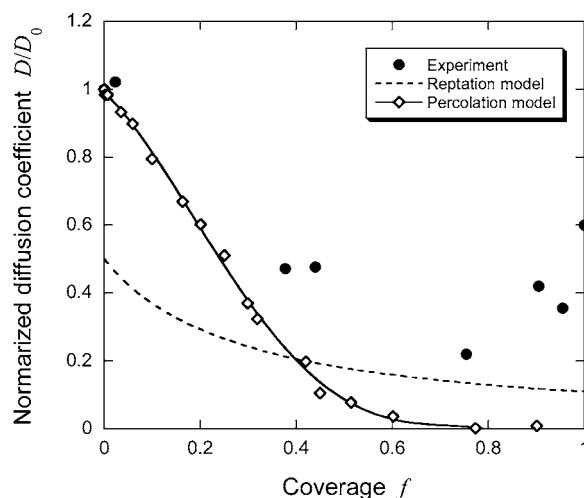

FIG. 4. Relationship between normalized diffusion coefficient of mobile molecule and coverage of bonded molecule (black circle). The average value of the diffusion coefficients after 20 and 24 h is plotted and D_0 is the diffusion coefficient for the lubricant film without annealing. The solid and broken lines are the calculated curves based on the percolation and reptation models. White diamonds are simulation results based on the percolation model and the solid line is a fitting curve.

cant are treated as free and frozen particles with equal size and the free particle cannot occupy the site when the site is already occupied by the frozen particle. The free particle makes its way through the frozen particles. This model can consider the random distribution of the bonded molecules and seems to be suitable for the explanation of the experiment. In Fig. 4, the calculated diffusion coefficients of a tracer free particle in a square lattice with blocked sites are plotted (white diamonds) and the solid line is the fitting curve of the calculated data by the least-squares method. The ratio of numbers of the vacant and blocked sites is assumed to be equal to the coverage of the experimental data, and D_0 is the diffusion coefficient without the background particles. The distribution of the blocked sites by the frozen particles were generated using random numbers generated by a computer and the free particle moves using the MC method, where it moves to a vacant site in every direction with a equal probability. The diffusion coefficients were obtained from the ratio of square displacement of the tracer particle and time. Lattice size was 250 000 sites, and the measured time was 500 MC steps, and the generated distribution patterns of the bonded molecules were 100. In addition, the data were the average data of 100 trials for the each pattern, that is, the number of the trial was 10 000 for one point in Fig. 4. The calculated results can explain the tendency of the experimental data at a small coverage (when f is less than around 0.5). In general, the diffusion coefficient should be zero at a larger coverage than a certain value in percolation models and the diffusion coefficient obtained by the simulation is almost zero at a coverage of more than around 0.6. On the other hand, the experimental values were not zero at a large coverage. These results indicate that the percolation model can explain the diffusion at a small coverage, however, it cannot at a large coverage.
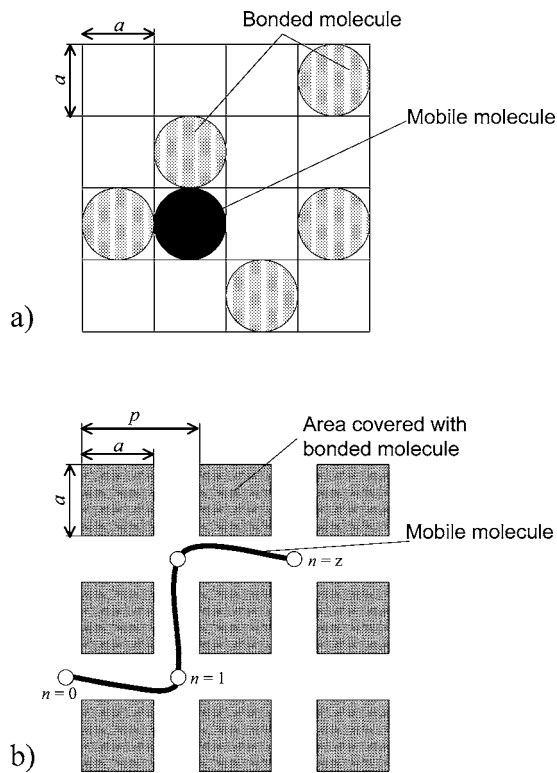
a)

b)

FIG. 5. Model for mobile and bonded molecules of submonolayer liquid polymer film. (a) percolation model and (b) reptation model.

Next, the reptation model is discussed [Fig. 5(b)]. In the percolation model, it is assumed that the mobile molecule is shaped like a particle or ball. Considering that the mobile molecules lie flat on the disk and the bonded ones lie less flat than the mobile ones as mentioned above, the mobile molecules should be shaped like a linear chain or snake. The mobile chain molecule moves through the bonded molecules. This mobile molecules should make their way by the lateral reptation motion. In the reptation model, the lateral motion of the molecule is highly constrained and it can move only along a virtual tube, which is made of the gap of the bonded molecules. This model seems to be suitable for the explanation of the diffusion at a large coverage. Although the bonded molecules distribute randomly, for simplicity, it is assumed that they distribute at a square lattice shown Fig. 5(b), where the pitch is p and the molecule shapes like a square with a size of $a \times a$. This model is the same as a standard lattice model for a reptation motion [24,25] and a model based on Ref. [25] is mentioned below. It is assumed that the mobile molecule jumps to the neighbor lattice point at a time interval of Δt. This means that the molecule moves a distance of p at a interval of Δt, and the mean square distance of the movement for the period of time t is $\langle s(t)^2 \rangle = (t/\Delta t)p^2$. The mean square distance can also be written as $\langle s(t)^2 \rangle = 2D_0 t$ using the diffusion coefficient D_0, where D_0 is the diffusion coefficient for the mobile molecule without the bonded molecules. Therefore the following relation can be obtained:

$$\Delta t = \frac{p^2}{2D_0}. \tag{8}$$

The mobile molecule lies flat on the disk and winds along the contour of the bonded molecules. Regarding the part of the molecule between the winding points as one segment [the winding points are small circles of the mobile molecule in Fig. 5(b)], the average number of segments z is given by

$$l = zp, \tag{9}$$

where l is the length of the mobile molecule. In this model, we can treat the mobile molecule as a linear chain molecule with z segments. Let the coordinate of the segment be $P_n(t)(n=0, 1, 2, \ldots, z)$. If the zth segment of the molecule moves, which is called the forward movement here, the coordinate $P_n(t+\Delta t)$ at $t=t+\Delta t$ is given by

$$P_n(t + \Delta t) = P_{n+1}(t). \tag{10}$$

It should be noted that every segment moves to the neighbor segment position in the reptation motion. In addition, $P_{z+1}(t)$ is written as

$$P_{z+1}(t + \Delta t) = P_z(t) + p e(t), \tag{11}$$

where $e(t)$ is the unit vector with a random orientation. The position of the center of gravity

$$P_G(t) = \frac{1}{z+1} \sum_{n=0}^{z} P_n(t). \tag{12}$$

Using Eqs. (10)–(12),

$$P_G(t + \Delta t) = \frac{1}{z+1} \left[\sum_{n=1}^{z} P_n(t) + P_{z+1}(t) \right]$$

$$= P_G(t) + \frac{1}{z+1} [P_{z+1}(t) - P_0(t)]$$

$$= P_G(t) + \frac{1}{z+1} [P_z(t) + p e(t) - P_0(t)]$$

$$= P_G(t) + \frac{1}{z+1} [P(t) + p e(t)] = P_G(t) + f(t), \tag{13}$$

where $P(t) = P_z(t) - P_0(t)$, which is a segment vector from the tail to head segments, and

$$f(t) = \frac{P(t) + p e(t)}{z+1}. \tag{14}$$

Because $P_G(t + \Delta t)$ is obtained in the same manner in the case of the backward movement, $P_G(t + \Delta t)$ can be generally written as

$$P_G(t + \Delta t) = P_G(t) + \xi(t) f(t). \tag{15}$$

Using Eqs. (15), the average displacement of the center of gravity over the large number of molecules is given by

$$\langle (\boldsymbol{P_G}(t) - \boldsymbol{P_G}(0))^2 \rangle = \frac{t}{\Delta t} \langle f(t)^2 \rangle. \tag{16}$$

Using $\langle \boldsymbol{P}(t)^2 \rangle = z\, p^2$,

$$\langle f(t)^2 \rangle = \frac{\langle \boldsymbol{P}(t)^2 \rangle + p^2}{(z+1)^2} = \frac{1}{z+1} p^2. \tag{17}$$

Moreover, using Eq. (8), Eq. (16) is rewritten as

$$\langle [\boldsymbol{P_G}(t) - \boldsymbol{P_G}(0)]^2 \rangle = \frac{2D_0}{z+1} t. \tag{18}$$

Furthermore, the relationship between $\boldsymbol{P_G}(t)$ and the two-dimensional diffusion coefficient D when the mobile molecule moves through the bonded ones can be written by

$$\langle [\boldsymbol{P_G}(t) - \boldsymbol{P_G}(0)]^2 \rangle = 4Dt. \tag{19}$$

From Eqs. (18) and (19), we get

$$D = \frac{1}{2} \frac{D_0}{z+1}. \tag{20}$$

Using the geometrical relationship [Fig. 5(b)], the coverage of the bonded molecule f can be written as

$$f = \left(\frac{a}{p} \right)^2. \tag{21}$$

Using Eqs. (9), (20), and (21), the relationship between the diffusion coefficient D of the mobile molecule and the coverage f of the bonded molecule can be obtained as

$$D = \frac{1}{2} \frac{D_0}{\frac{l}{a}\sqrt{f} + 1}. \tag{22}$$

Note that the diameter of the bonded molecule a depends on the coverage f as mentioned in Sec. III A, $a(f)/a_{\min}$ can be experimentally obtained by using the result that $a/a_{\min} = \beta/\sqrt{f}$. The coefficient β can be obtained from the results shown in Fig. 2. Moreover, $a_{\min}$ was estimated as mentioned below. Assuming that the bonded molecule when $b=1$ is shaped like a circular plate (diameter: $a_{\min}$; thickness: h) and the volume of the circular plate-shaped molecule is as large as that of the bulk, the following relationship is valid:

$$\frac{4}{3} \pi r_G{}^3 = \pi \left(\frac{a_{\min}}{2} \right)^2 h, \tag{23}$$

where r_G is the molecular radius of the gyration. Using Eq. (23) and the results that the monolayer thickness was 1.4 nm

as shown in Fig. 1(b), $a_{\min}$ is about 3.6 nm. Thus the ratio of $l/a_{\min}$ can be also theoretically obtained as $l/a_{\min} = 3.9$. Substituting $a(f)(=a_{\min}\beta/\sqrt{f})$ to Eq. (22), the calculated results are plotted in Fig. 4. The calculated results can explain the tendency of the experimental data at a large coverage (when $0.6 < f < 0.9$), whereas it is different from the experimental data both at a small coverage and at around 1. The diffusion coefficients when f is around 1 take larger values than the theoretical ones. This may be because more mobile molecules move on the bonded molecules and fewer move through the bonded molecules, to which the two models are applicable. Thus the tendency of the experimental results can be explained by the percolation model at a small coverage and it can be explained by the reptation model at a large coverage. This indicates that the mobile and bonded molecules can be approximated to be particles whose conformation can be neglected at a small coverage, whereas the model should include the conformation as the reptation model at a large coverage. In addition, it should be noted that the experimental values are larger than the theoretical ones. In both two models, the mobile molecule cannot pass through the areas occupied by bonded molecules. The larger diffusion coefficients may suggest that the mobile molecule is not completely blocked by the bonded ones. Further investigation is necessary to establish a more accurate model, although two models can explain the tendency of the experimental results.

IV. SUMMARY

We investigated the spreading of the submonolayer liquid polymer films on solid surface that consist of the molecules with different mobilities. From the measurement of the dispersive surface energy, a mobile molecule lies flat on the disk surface and a bonded molecule lies less flat than a mobile one. In addition, the relation between the diffusion coefficient of the mobile molecule and the coverage of the bonded one can be explained by the percolation model at a small coverage and it can be explained by the reptation model at a large coverage.

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