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Complex terraced spreading of perfluoropolyalkylether films on carbon surfaces

X. Ma,[1,*] J. Gui,[2] L. Smoliar,[2,†] K. Grannen,[2] B. Marchon,[2,‡] C. L. Bauer,[1] and M. S. Jhon[3]
[1]*Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213*
[2]*Seagate Recording Media Group, 47010 Kato Road, Fremont, California 94538*
[3]*Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213*

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Complex molecular layering of OH-terminated perfluoropolyalkylether films over amorphous carbon surfaces has been observed using spatially resolved microellipsometry. The first layer is diffusive in nature, and the subsequent layers exhibit sharp steps of about twice the thickness of the first layer. This behavior, characteristic of a coexisting two-dimensional gas, with cohesive, liquidlike multilayers, is in clear contrast with that of the CF_3-terminated analog, which shows a smooth diffusive profile. In this particular case, spreading, for thickness greater than one monolayer, can be exactly described by a Poiseuille flow in a disjoining pressure gradient originating solely from van der Waals interactions. For both types of polymers, diffusion rate reaches a maximum at full monolayer coverage, and decreases in the submonolayer regime. Spreading for both types of polymers unambiguously follows a $t^{1/2}$ time dependence. [S1063-651X(99)05601-9]

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I. INTRODUCTION

Recently, the spontaneous spreading of liquid films on solid surfaces on the microscopic scale has gained considerable interest, in part because a fundamental understanding of the interactions between liquid molecules and solid surfaces that govern spreading has technological applications, such as in molecular boundary lubrication of magnetic recording media.

The spreading behavior of small drops of polydimethylsiloxane (PDMS) on solid surfaces has been intensively studied by Heslot, Fraysse, and Cazabat [1,2], Cazabat *et al.* [3], and Valignat *et al.* [4]. They reported that for PDMS terminated with trimethyl groups on silica, molecular layering develops with a layer thickness of around 0.7 nm. However, PDMS terminated with hydroxyl groups did not show molecular layering, and an anchored layer with a thickness close to the gyration radius was observed. Novotny [5] has investigated the spreading of polyperfluoropropylene oxides (PPFPO) on silica surfaces using scanning microellipsometry and scanning photoemission spectroscopy. No molecular layering was reported for this system. The spreading behavior of perfluoropolyalkylethers (PFPE's) on silica surfaces as a function of end group functionality, molecular weight, temperature, and humidity has been studied by O'Connor and co-workers [6,7], and Min *et al.* [8]. They observed the development of an anchored layer from difunctional PFPE's such as *Z*dol (terminated with hydroxyl groups), AM2001 (pyperonyl groups), and *Z*tetraol (propylene glycol ether groups). Multiple layers were not reported for these systems. In this work, the spreading behavior of PFPE's with and without reactive end groups on amorphous carbon surfaces was studied. A complex layered structure in the spreading profiles for OH-terminated PFPE films has been observed. To our knowledge, this complex molecular terracing has not been reported before.

Many authors, based on both experimental work and simulations, have discussed the time dependence of molecular spreading. Layering behavior of polymer liquids has already been observed, with the front of the layers moving with a $t^{1/2}$ dependence [1,2]. O'Connor and co-workers observed two different time dependencies for the movement of a polymer liquid front: the movement was linearly dependent on time at short times and a $t^{1/2}$ dependence was found for long times [6,7]. The two-regime picture of spreading is supported by Monte Carlo simulations of Lukkarinen, Kasha, and Abraham [9] and molecular-dynamics simulations of Nieminem *et al.* [10]. Simulations by Burlatsky *et al.* report a $t^{1/2}$ dependence but do not break down the spreading into two time regimes [11]. In a molecular-dynamics simulation by Yang, Koplik, and Babavar a $(\log_{10} t)^{1/2}$ dependence was found for a simple (i.e., atomic or diatomic) three-phase Lennard-Jones system [12]. When this model was modified for long chain molecules, however, a $t^{1/2}$ dependence was observed [13,14]. The experimental determination of the time dependence of the polymer front movement requires that a ''front'' be defined. Since the interface of the liquid polymer with the solid surface in a submonolayer regime (two-dimensional gas) is asymptotic, the definition of the ''front'' is somewhat unclear, and in the case where it is defined as the position of the most distant particle, or boundary particle [11], it is almost impossible to accurately determine experimentally. In the present work, a front is not explicitly defined, and instead, the thickness-dependent diffusion is extracted numerically from the film thickness profiles [15].

II. EXPERIMENT

The liquid polymers used in this work are monodispersed PFPE's: *Z*dol and *Z*03, which have a similar main-chain structure as

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[*] Present address: Seagate Recording Media, 47010 Kato Rd., Fremont, CA 94538.

[†] Present address: 3D Technology Laboratories, Inc., 200 Blossom La., Mountain View, CA 94041.

[‡] Present address: IBM, Almaden Research Center, 650 Harry Rd., San Jose, CA 95120.

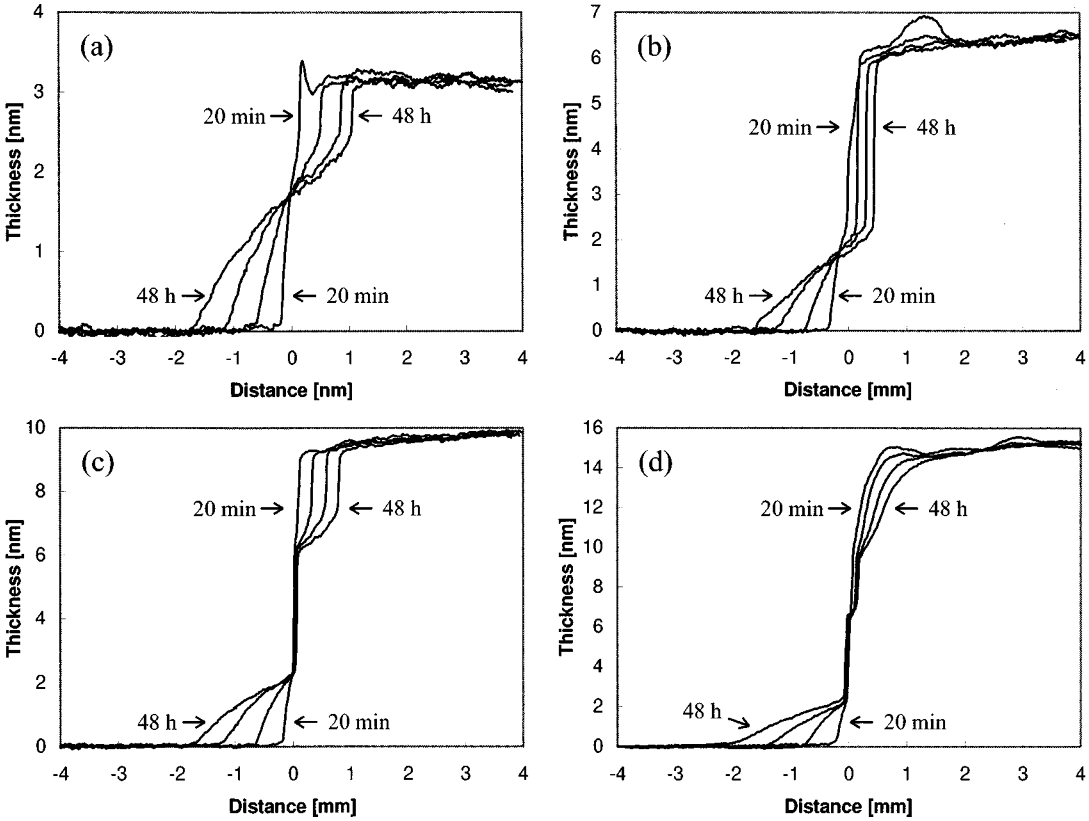

FIG. 1. Spreading profiles of *Z*dol with different initial thickness, at times of 20 mn, 7 h, 24 h, and 48 h.

$$X-\mathrm{CF}_2-[(\mathrm{OCF}_2-\mathrm{CF}_2)_n-(\mathrm{OCF}_2)_m]-\mathrm{OCF}_2-X,$$

where $X=\mathrm{CH_2OH}$ and $n/m \cong 1$ for *Z*dol, and $X=\mathrm{F}$ and $n/m \cong \frac{2}{3}$ for *Z*03. The molecular weight M_n and polydispersity are 2500 g/mol and 1.04 for *Z*dol, and 2500 g/mol and 1.54, respectively, for *Z*03. The amorphous carbon surfaces were prepared by dc magnetron sputtering onto highly polished nickel-phosphorus coated aluminum substrates. The average roughness of the substrate surface is less than 0.6 nm, as measured by atomic force microscopy (AFM). The thickness of the amorphous carbon layer is about 20 nm, which is sufficiently thick to screen out the effect of the substrate. In order to create a sharp boundary of the polymer film, the disk was partially immersed in a dilute perfluorohexane solution, and was withdrawn from the solution at a constant speed. The initial film thickness was controlled by adjusting the solution concentration and the withdrawing speed [16].

The time-dependent thickness profiles of the films were measured using a PLASMOS SD400 scanning ellipsometer system equipped with microprobe optics. The spot size of the He-Ne laser beam (632.8 nm) at an angle of incidence of 70° was $10 \times 35\ \mu\mathrm{m}^2$. The translational x-y sample stage has a lateral resolution of 2 μm. The sample was oriented such that the polymer film boundary was parallel to the plane of incidence. The scanning step size used in this experiment was 20 μm. The accuracy and reproducibility of film thickness measurement for this system was less than 0.1 nm. The measurements were performed at ambient temperature (~26 °C) and under a dry nitrogen atmosphere.

III. RESULTS AND DISCUSSION

The time-dependent thickness profiles of *Z*dol with different initial thickness are shown in Fig. 1. The spreading of *Z*dol results in a stepped thickness profile. For films with initial thicknesses of 3.2 and 6.5 nm, a distinct layer with a height of 2.2 nm extends out of the main liquid front. For thicker *Z*dol films with initial thicknesses of 9.8 and 15 nm [Figs. 2(c) and 2(d)], several steps become very distinct after a few hours of spreading. On the top of the first layer, a second, even a third layer can be readily identified. The thickness is about 2.2 nm for the first layer, 4.2 nm for the second layer, and 3.4 nm for the third layer. Within the first three layers, only the first one has a gradual (diffusive) profile. Both the second and the third layers develop abrupt stepwise profiles.

O'Connor and co-workers [6,7] have reported a shoulder layer developing from *Z*dol and AM2001 films on silica surfaces. Similar observations were also reported by Valignat *et al.* [4] for the hydroxyl-terminated polydimethylsiloxane (PDMS-OH) on silica surfaces. This shoulder was interpreted as the anchoring of the OH ends of the polymer on the available silanol groups of the silica surfaces. The height of the shoulder was found to be close to the gyration diameter of the polymer in bulk, which infers that the molecules on the surface have a conformation close to that of the bulk. In both cases, no multiple layering was reported. Spreading profiles with multiple layers have been reported, however, by Heslot and co-workers [1,2] for PDMS and tetrakis (2-ethylhexoxy)-silane on silica. They found that all the layers had the same thickness of approximately 0.7 nm, corre-

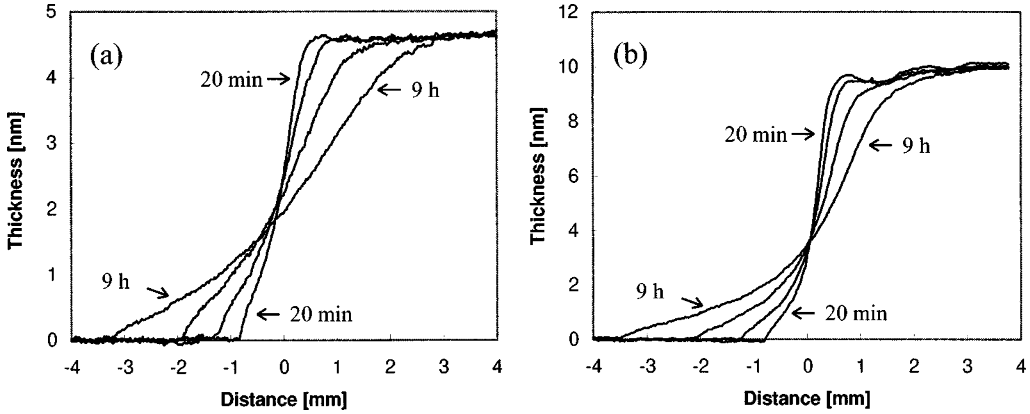

FIG. 2. Spreading profiles of *Z*03 with different initial thickness, at times of 20 mn, 1 h, 3 h, and 9 h.

sponding to the cross-sectional diameter of the polymer chain. In our case, we have observed multiple layers developing from the liquid front, but each layer exhibits a different thickness. The thickness of the first layer is close to the diameter of gyration of the polymer in bulk, which agrees with O'Connor's results [16]. It is worth noticing that the thickness of the second layer is nearly twice the thickness of the first layer. This could suggest that this second layer consists of polymer molecules attached end to end with their end groups bound together via hydrogen bonding (dimers). In a recent study, Tyndall [17] measured *Z*dol surface energy as a function of film thickness on amorphous carbon. He reported that the polar component of the surface energy goes through several minima, with the distance between the first and the second minimum being about twice the thickness corresponding to the first minimum. Their results agree with our observations and they might provide us with further evidence of the conformation of the molecules on the carbon film.

The spreading profile of *Z*03, which has the same main chain structure as *Z*dol but is terminated with nonfunctional CF_3 end groups, contrasts sharply with those of *Z*dol. As shown in Fig. 2, no layered structure is observed. Instead, the liquid front evolves smoothly with time, leading to a gradual and diffusive profile. This type of profile was also observed by O'Connor and co-workers for the same polymer, on silica surfaces [6,7]. It clearly suggests that the OH groups are responsible for the development of the layered spreading profile of *Z*dol.

The spreading of thin liquid films on solid surface, with the thickness approaching molecular dimensions, can be treated as a process controlled by surface diffusion [5]. The driving force for the diffusion process is the gradient of disjoining pressure that results from the gradient in film thickness [18]. In previous studies [1–4,6–8], the surface diffusion coefficient was extracted from the measurement of the movement of the leading edge of the film, using the relation $x \sim t^{1/2}$. Its determination was therefore highly dependent on the definition and the measurement of the leading edge. In addition, because this diffusionlike coefficient was in fact calculated from the measured flow rate, its value depended on the initial film thickness. In order to overcome these limitations, the Matano Interface method [15] was employed throughout this work, which extracts the thickness-dependent diffusion coefficient directly from the film profile. Since the spreading is measured in the direction perpendicular to the film boundary, the spreading process can be described by a one-dimensional diffusion equation as

$$\frac{\partial h(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D(h) \frac{\partial h(x,t)}{\partial x} \right), \tag{1}$$

where $h(x,t)$ is the thickness of the film at a distance x from the initial film boundary at time t (note that this thickness is not the film initial thickness), and $D(h)$ is the thickness-dependent diffusion coefficient. The integration of Eq. (1) under the sharp initial film boundary condition gives

$$D(h) = -\frac{1}{2t}\left(\frac{dx}{dh'} \right)_{h'=h} \int_0^h x\,dh' \tag{2}$$

with the condition

$$\int_0^{h_0} x\,dh' = 0. \tag{3}$$

Therefore, the value of $D(h)$ as a function of film thickness can be determined experimentally from a measured thickness profile by using Eqs. (2) and (3).

Figure 3 shows the diffusion coefficient $D(h)$ as a function of film thickness h for a 15-nm-thick *Z*dol film. These three curves were calculated from the spreading thickness profiles measured at different times after coating. These

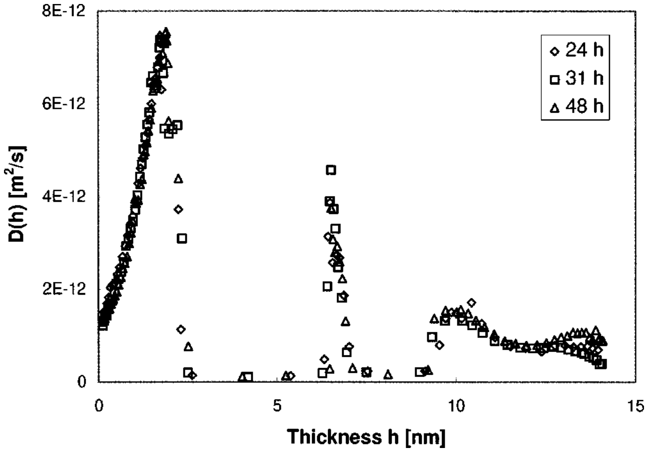

FIG. 3. Diffusion coefficient $D(h)$ vs lube thickness for *Z*dol at three different times.

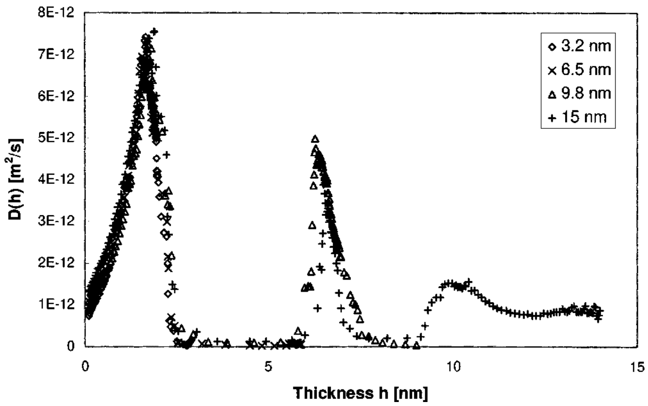

FIG. 4. Diffusion coefficient $D(h)$ vs lube thickness for Zdol for four different initial thicknesses.

curves overlap with each other, implying that $D(h)$ is independent of time. Since Matano's formalism uses a $x/t^{1/2}$ variable transformation, the independence of $D(h)$ curves with time proves indirectly, but unambiguously, that the spreading has a $t^{1/2}$ dependence. Our limited spatial and time resolution did not allow us, however, to explore shorter time behavior of less than 30 mn. Therefore, we did not access the first spreading regime discussed by O'Connor and co-workers [6,7], Lukkarinen, Kashi, and Abraham [9], and Nieminem, *et al.* [10]. We have measured profiles as long as a week after coating, and we find that the $D(h)$ profiles remain unchanged. The diffusion coefficient curves for Zdol films of different initial thickness are plotted in Fig. 4. These profiles again overlap with each other for different initial film thickness, which confirms that $D(h)$ is indeed also independent of the initial film thickness.

For Zdol, the diffusion coefficient increases initially as the film thickness increases, and it reaches a maximum at the thickness of 1.7 nm. It then drops abruptly to nearly zero, and subsequent maxima at approximately 6.5 and 10 nm are also observed. These successive maxima are typical of highly cohesive, liquidlike molecular layers. After going through the third maximum, $D(h)$ does not drop to zero, but maintains at a small, finite value. The peak $D(h)$ value corresponding to each successive maximum becomes lower with increasing thickness. This suggests that the molecular layering effect diminishes as the film thickness increases, approaching bulk properties.

Z03 also exhibits $D(h)$ profiles that are both independent of initial film thickness and time. However, its spreading behavior is in sharp contrast with that of Zdol. An example of $D(h)$ curves for two different thicknesses is shown in Fig. 5. $D(h)$ initially also increases as the film thickness increases, but that it reaches its maximum value at a lower thickness of 1 nm. Thereafter, $D(h)$ decreases monotonically with increasing film thickness, and it closely follows a $1/h$ relationship, as shown in Fig. 6. Previous studies on the spreading of liquid films in the hydrodynamic range (Poiseuille flow) have shown that if the disjoining pressure arises solely from van der Waals interactions, the diffusion coefficient should be inversely proportional to film thickness as [19,20]:

$$D(h)=A_H/6\pi\eta h, \tag{4}$$

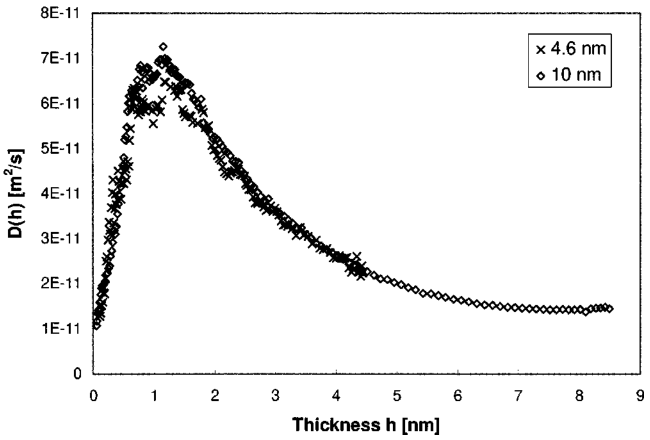

FIG. 5. Diffusion coefficient $D(h)$ vs lube thickness for Z03 for two different initial thicknesses.

where A_H is Hamaker constant, and η is the viscosity of the liquid. The fact that $D(h)$ of Z03, for $h>1$ nm, is proportional to $1/h$ implies that van der Waals interaction is the dominant driving force for Z03 spreading on the amorphous carbon, at least for the thickness greater than a monolayer. For Z03 at room temperature, $\eta \cong 0.06$ Pa s [21], which allows an estimation of the Hamaker constant for this system at $A_H = 1.1\times10^{-19}$ J. This value is within the order of magnitude of Hamaker constant for liquid film on solid surfaces [22]. For highly cohesive films such as Zdol, the spreading profiles develop a layered structure, and the hydrodynamic theory is no longer suitable. In addition, the polar term in the expression of the disjoining pressure can no longer be neglected. A new approach, such as the one proposed by de Gennes and Cazabat [23], and Bruinsma [24] should therefore be considered, where a friction term arises from the interactions between the molecules and the solid surface, and also from the interactions among the molecules of the neighboring layers.

The maximum $D(h)$ value for Z03 is nearly one order of magnitude higher than that of Zdol, suggesting that the functional end-groups of Zdol significantly retard the diffusion process, owing probably from their stronger interactions with the carbon surface. In addition, it is worth noticing that the thickness at which $D(h)$ reaches the maximum is close to the cross sectional diameter of the main chain of the Z03 mol-

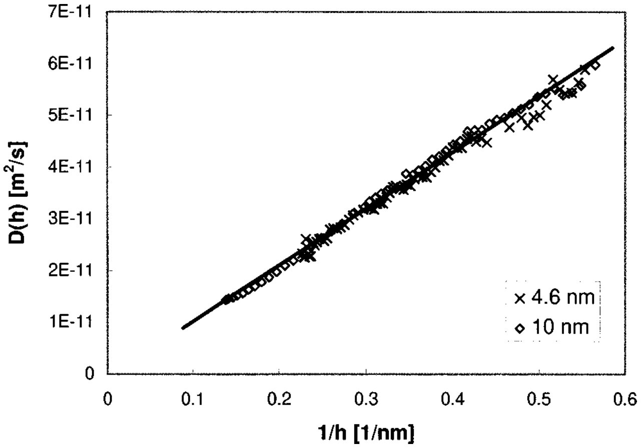

FIG. 6. Diffusion coefficient $D(h)$ vs $1/h$ for Z03.

ecules (~0.7 nm), whereas for *Z*dol, it is close to the diameter of gyration ($2R_g$) of the molecule (~2.4 nm) [16]. This might suggest that for *Z*03, the absence of functional end groups makes the molecules of the first monolayer lie flat on the surface, whereas for *Z*dol, the strong interaction of the OH-end groups with the carbon surface leads to a conformation with one or both ends attaching to the surface and the main-chain standing out of the surface with a height on the order of $2R_g$ [25,26]. Further experimental evidence for this hypothesis, using polymer chains of various lengths (molecular weight) will be reported in a separate paper.

When the film thickness for both *Z*dol and *Z*03 is less than one monolayer the $D(h) \propto 1/h$ relationship definitely breaks down, and it is unclear at this point how $D(h)$ should behave as h approaches zero. Novotny [5] has suggested that $D(h)$ should remain constant in the submonolayer regime, which is obviously in contradiction with our results. One possible explanation could lie in the fact that the surface of the amorphous carbon under investigation is populated with surface sites of different interaction strengths, with the strong sites being associated with higher binding energy [27]. When PFPE molecules start to be adsorbed on the surface, they first occupy the strong sites (sites of higher energy). Since the characteristic hopping time between two strong sites must scale with higher activation energy, the diffusion process will be slower at lower coverage. As more molecules are adsorbed, weaker sites (sites of lower energy) start to be populated, and the diffusion process speeds up as molecules are now adsorbed on the sites with lower hopping times. A quantitative model based on this hypothesis is currently under development, and will be published separately.

IV. SUMMARY

We have reported ellipsometric measurements of the spreading of PFPE thin films on amorphous carbon surfaces. Layers of various thicknesses were observed for OH terminated PFPE (*Z*dol). The first layer thickness is close to the diameter of gyration of *Z*dol in the bulk, and the second layer thickness is roughly twice that of the first layer. No layered structure was observed for CF_3 terminated PFPE (*Z*03). The Matano interface method was employed to extract the thickness-dependent diffusion coefficient $D(h)$, which proved independent of time and initial film thickness. This implies that the spreading of *Z*dol and *Z*03 on amorphous carbon follows a $t^{1/2}$ dependence. The $D(h)$ versus h curve for *Z*dol shows several peaks corresponding to the layered structure in the thickness profiles. A near zero diffusion coefficient occurs at the thickness values in between peak positions, corresponding to the abrupt and nearly stationary steps on the liquidlike film thickness profile. The diffusion coefficient of *Z*03 only has one peak at a thickness corresponding roughly to the cross-sectional diameter of the molecules. These results suggest that the molecular orientation of PFPE on amorphous carbon surface depends strongly on the functionality of its end groups. In addition, the end groups play a very important role in determining the surface mobility of these molecules. With nearly the same main chain structure and the same size, *Z*dol, terminated with OH groups, spreads close to one order of magnitude slower than *Z*03, which is terminated with CF_3 groups. For both types of molecules, the thickness-dependent diffusion coefficient decreases as film thickness decreases, when the film thickness is below one monolayer, owing possibly to a distribution of sites with various interaction strengths.

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