

Microscopic Spreading of Nonreactive Perfluoropolyalkylether Film on Amorphous Carbon Surfaces

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Abstract—A spreading mechanism of nonfunctional perfluoropolyalkylether (PFPE) on carbon surfaces is proposed. For the thin thin-film regime, adsorption-desorption is a main driving force for spreading, and the surface diffusion coefficients increase as the film thickness increases. A two-dimensional virial equation is employed to explain the dependency of surface diffusion coefficient on the film thickness. For the thick thin-film regime, the spreading characteristic is determined by the disjoining pressure gradient. We adopt a slip boundary condition to analyze the thick thin-film regime. This modification of the boundary condition reasonably explains the dependence of surface diffusion coefficients on film thickness.

Key words: Microscopic Spreading, Surface Diffusion, PFPE, Partial Slip Effect

INTRODUCTION

The spreading of liquid films on solid surfaces in the macroscopic regime has been extensively investigated [Teletzke et al., 1987]; however, microscopic spreading behavior is quite different from the macroscopic case. At the microscopic scale for a film thickness less than 10 nm, the spreading is governed by the forces originating from the disjoining pressure gradient [Mate, 1992]. The spreading behavior of small drops of polydimethylsiloxane (PDMS) on silica surfaces has been intensively studied by Heslot et al. [1989], Cazabat et al. [1990], Valignat et al. [1993], and Fraysse et al. [1993]. Although several theoretical efforts attempt to explain the experimental observations [Mate, 1992; Cazabat et al., 1990], an understanding of microscopic spreading of liquid film is still needed.

The spreading of ultra-thin, polymer lubricant films on solid surfaces has attracted considerable interest due to its application in the lubrication of magnetic recording media. Novotny [1990] has investigated the spreading of polyperfluoropropylene (PPFPO) on silica surfaces using scanning micro-ellipsometry and scanning photoemission spectroscopy. The surface diffusion coefficient increased as the film thickness decreased down to 1 nm, and was constant below this value. The spreading characteristics of perfluoropolyalkylethers (PFPE) on silica surfaces has been investigated as a function of initial film thickness, end group functionality, molecular weight, temperature and humidity by Min et al. [1995], O'Connor [1995] and Ma [1998] using scanning micro-ellipsometry. They extract the surface diffusion coefficients from the spreading profiles by employing Matano interface method [Matano, 1993].

In present work, the spreading of nonfunctional PFPE on carbon surfaces was studied. We analyzed the surface diffusion coefficients in two separate regimes. For the thicker regime, a hydro-

dynamic approach with a slip boundary condition was applied. For the thinner regime, we assumed adsorption-desorption is the main mechanism for spreading. We explain the dependence of surface diffusion coefficients on film thickness systematically.

THEORETICAL ANALYSIS

It is well known that the driving force for microscopic spreading is the disjoining pressure gradient along the spreading direction. For film thickness greater than several monolayers (thick thin-film), conventional hydrodynamics are assumed to be valid [Mate, 1992]. However, for film thickness less than a monolayer (thin thin-film), adsorption and surface pressure play important roles in spreading [Cazabat, 1990]. In the intermediate range, we assume the hydrodynamic analysis with slip effects is applicable. The velocity field in a spreading film is shown in Fig. 1.

If the liquid in the film can be treated as a Newtonian fluid, the Navier-Stokes equation is used as a governing equation of motion for the relatively thick film in the following form, under the pseudo steady state approximation [Mate, 1992]:

$$-\eta \frac{\partial^2 v}{\partial z^2} = \frac{\partial \Pi}{\partial x} \quad (1)$$

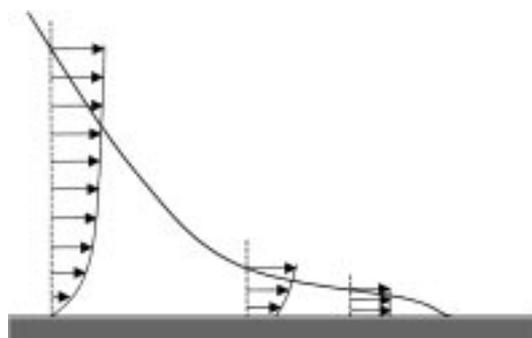


Fig. 1. Schematic representation of velocity fields.

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where η is the viscosity of liquid, v is the velocity in the x direction, and Π is the disjoining pressure. At the solid-liquid interface, the following boundary condition is assumed instead of the conventional no-slip condition [Bird et al., 1960]:

$$\frac{\partial v}{\partial z} = \beta v \quad \text{at } z=0 \quad (2)$$

The conventional no-slip condition at solid-liquid interface is constructed by setting $\beta \rightarrow \infty$. If the liquid film is composed of long chain polymer, the molecules can become entangled. The entanglement can create a finite slip at the solid-liquid interface. In this case, β has a positive finite value. If the liquid molecules are attached to the solid surface, the attached molecules can reduce the conductance of molecularly thin liquid film. In this case, β has a negative finite value. At the liquid-air interface, the following stress-free condition is applicable:

$$\frac{\partial v}{\partial z} = 0 \quad \text{at } z=h \quad (3)$$

The velocity profile satisfying the above Eqs. (1)-(3) is

$$v(z) = \frac{1}{\eta} \left(\frac{h}{\beta} + hz - \frac{z^2}{2} \right) \frac{\partial \Pi}{\partial x} \quad (4)$$

This velocity field is shown in Fig. 2. By adjusting the value of β , we can get velocity profiles given in Fig. 6 of Mate's [1992] work. The associated flow rate, q , is

$$q = \int_0^h v(z) dz = \frac{1}{\eta} \left(\frac{h^2}{\beta} + \frac{h^3}{3} \right) \frac{\partial \Pi}{\partial x} \quad (5)$$

The disjoining pressure, $\Pi = (\partial F / \partial h)_\eta$, is the excess pressure arising from the interactions between a solid surface and liquid molecules. For a liquid with non-reactive end group, the interaction between solid surface and liquid molecules is assumed to be governed by van der Waals interactions; then, the disjoining pressure has the following form [Tabor and Winterton, 1968]:

$$\Pi = \frac{A}{6\pi h^3} \quad (6)$$

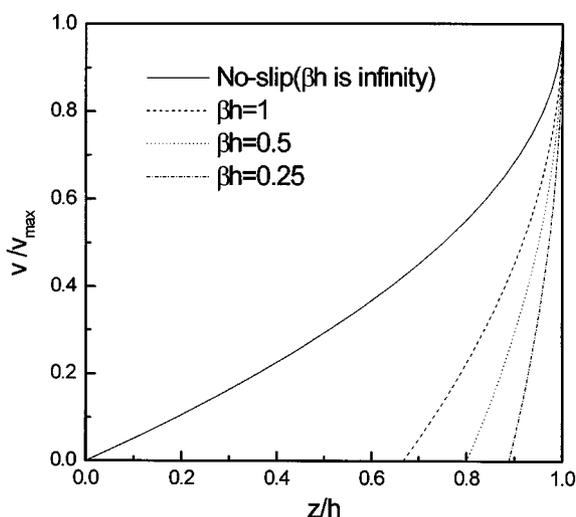


Fig. 2. Velocity profiles for various βh .

The above relation explains that disjoining pressure decreases rapidly as the film thickness, h increases. In this case, the flow rate is

$$q = - \frac{A}{6\pi\eta h^4} \left(\frac{1}{h} + \frac{3}{\beta h^2} \right) \frac{\partial h}{\partial x} \quad (7)$$

It is known that thin films flow faster than thick films for a particular gradient in film profile, $\partial h / \partial x$, and the thinner the films are, the more pronounced slip effects are.

In the general case, the continuity equation is written as, under the pseudo-steady state approximation,

$$\frac{\partial h}{\partial t} = - \frac{\partial q}{\partial x} \quad (8)$$

By combining Eqs. (7) and (8), we obtained the following surface diffusion equation:

$$\frac{\partial h}{\partial t} = \frac{A}{6\pi\eta} \frac{\partial}{\partial x} \left[\left(\frac{3}{\beta h^2} + \frac{1}{h} \right) \frac{\partial h}{\partial x} \right] \quad (9)$$

which is also expressed as

$$\frac{\partial h(x, t)}{\partial t} = \frac{\partial}{\partial x} \left[D_s(h) \frac{\partial h(x, t)}{\partial x} \right] \quad (10)$$

where the quantity $D_s(h) = (A/6\pi\eta)[3/\beta h^2 + 1/h]$ can be interpreted as a thickness-dependent surface diffusion coefficient. As the film thickness increases, the slip effects become negligible and the surface diffusion coefficient has the form of $D_s(h) = (A/6\pi\eta h)$, which is derived from the no-slip condition. It is assumed that the molecular weight effect on surface diffusion coefficient is implied in η . The dependency of zero shear viscosity $[\eta]_0$ on the molecular weight has the following forms [Marchionni et al., 1990]:

$$[\eta]_0 \propto M_w^{1.5} \quad (M_w < M_c)$$

$$[\eta]_0 \propto M_w^{2.5} \quad (M_w > M_c)$$

with the critical molecular weight $M_c \approx 15,000$. The exponents of 1.5 and 2.5 are quite different from those of the majority of polymer melts, which are 1 and 3.4, respectively [Ferry, 1970]. Therefore, we can assume that the dependency of the surface diffusion coefficient on the molecular weight has the form of $D_s \propto M_w^{-2.5-1.5}$.

For the sub-monolayer regime, the friction term cannot be calculated with the above hydrodynamic theory. Instead it is decided from the friction between molecule and solid surface. The velocity, v_m , for this regime can be written as [Cazabat et al., 1990]

$$v_m = \frac{V_M \partial \Pi}{\alpha \partial x} \quad (11)$$

where V_M is the molecular volume and α is the friction coefficient between the molecule and the surface. This relationship is quite similar to Darcy's law for flow through porous media. The resistance term of this relationship, α/V_M , corresponds to that of Darcy's law η/K . There are some models for the friction coefficient, α [Bruinsma, 1990]; however, rigorous models have not been developed. The corresponding sub-monolayer surface diffusion coefficient D_M can be obtained by employing the similar procedure of Eqs. (5) and (10), as:

$$D_M = - \frac{V_M h}{\alpha} \frac{\partial \Pi}{\partial h} \quad (12)$$

For thin films, the two-dimensional pressure $P(h)$ is commonly used for describing monolayers. This pressure is correlated with the disjoining pressure as follows [Adamson, 1990]:

$$P(h) = -h\Pi(h) + \int_0^h \Pi(h) dh \quad (13)$$

Therefore, the sub-monolayer surface diffusion coefficient is expressed as

$$D_M = \frac{V_M \partial P}{\alpha \partial h} \quad (14)$$

For the ultra thin film ($h \rightarrow 0$), $P(h)$ is given by the two dimensional perfect gas law, as follows:

$$PS = kT \quad (15)$$

where S is the molecular area. The equivalent film thickness can be expressed as:

$$h = \frac{V_M}{S} \quad (16)$$

By combining the Eqs. (14)-(16), the limiting value for D_M can be obtained as

$$D_0 = D_M(h \rightarrow 0) = kT/\alpha \quad (17)$$

This value corresponds to the diffusion coefficient of an isolated molecule on the surface. For the thicker case, we employ the two-dimensional virial equation as the equation of state for the thin film:

$$\frac{PS}{kT} = 1 + \frac{B}{S} + \frac{C}{S^2} + \dots \quad (18)$$

where B and C are the first and second virial coefficients. By combining Eqs. (14) and (18), and neglecting higher order terms, the following relation is assumed to be good approximation of the surface diffusion coefficient for the sub-monolayer regime:

$$D_M = \frac{kT}{\alpha} \left[1 + \frac{2B}{S} h \right] \quad (19)$$

It is well known that the first virial coefficient, B , has the relation of $B \propto S$. In this case, the above relation for the surface diffusion coefficient in the sub-monolayer region is expressed as

$$D_M = \frac{kT}{\alpha} [1 + \gamma h] \quad (20)$$

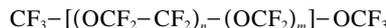
where γ is a constant that is independent of molecular weight. The molecular weight dependence on surface diffusion coefficients is implied in α . If it is assumed that the friction factor coefficient between surface and molecule, α , is proportional to the area which the molecule contacts the surface, the dependency of surface diffusion coefficients in this regime depends on the molecular conformation on solid surfaces.

Novotny et al. [1989] suggested that the surface conformation of polyperfluoropropylene oxide (PPFPO) is different from the bulk conformation. A two-layer model with interfacial and bulk layers was proposed: The interfacial layer, with a thickness of 1-2 monolayers, has the molecular chains preferentially extended along the surface. The remaining second layer has a normal bulk poly-

mer conformation. According to their suggestion the friction coefficient, α , is nearly proportional to molecular weight of each polymer, so the surface diffusion coefficient shows the relation of $D_s \propto M^{-1}$.

COMPARISON WITH EXPERIMENTS

The polymeric liquid used in this work is PFPE Z, which has the following chemical structure:



where $n/m \approx 2/3$. The physical properties of PFPE Z are summarized in Ma's [1998] work. The spreading profile of PFPE Z on an amorphous carbon surface was measured by using scanning micro-ellipsometry. Typical spreading profiles are given in Fig. 3. To extract the surface diffusion coefficients, the Matano Interface method [Matano, 1933], which extracts the thickness-dependent diffusion coefficient directly from the film profile, was employed.

Since the spreading is measured in the direction perpendicular to the film boundary, the spreading process is described by a one-dimensional diffusion equation as:

$$\frac{\partial h(x, t)}{\partial t} = \frac{\partial}{\partial x} \left[D_s(h) \frac{\partial h(x, t)}{\partial x} \right] \quad (10)$$

where $h(x, t)$ is the thickness of the film at a distance x from the initial film boundary at time t , and $D(h)$ is the thickness-dependent diffusion coefficient. The integration of Eq. (10) under the sharp initial film boundary condition gives:

$$D_s(h) = -\frac{1}{2t} \left(\frac{dx}{dh} \right)_{h'=h} \int_0^h x dh' \quad (21)$$

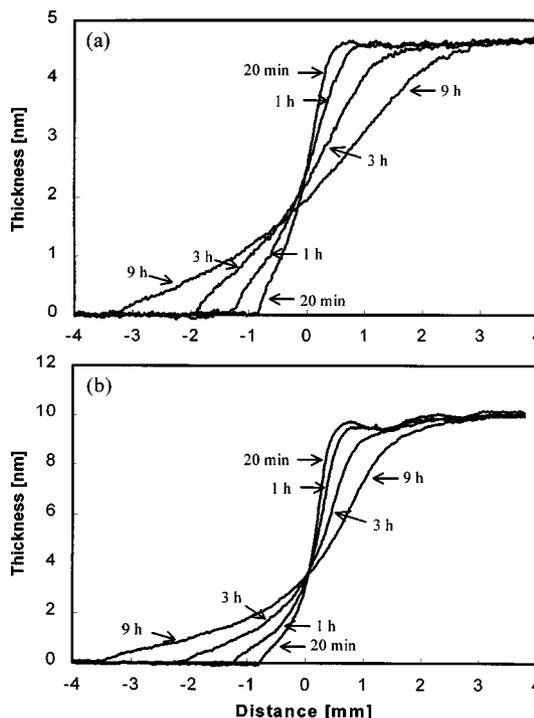


Fig. 3. Thickness profiles of Z ($M_n = 2,500$ g/mol) with the initial thickness of (a) 4.6 nm, and (b) 10 nm at 20 min, 1 h, 3 h, and 9 h.

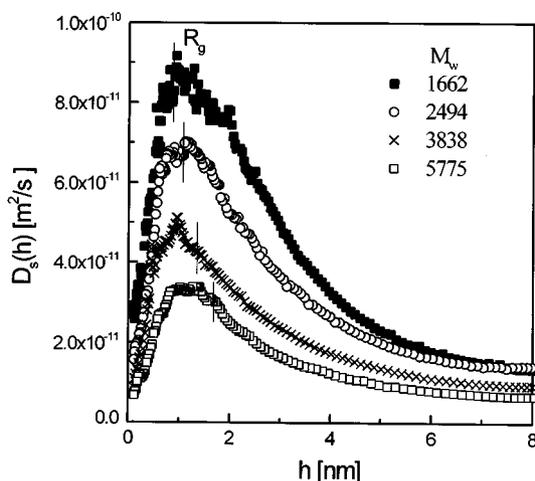


Fig. 4. Experimental data of surface diffusion coefficient of PFPE-Z [Ma, 1998].

with the condition:

$$\int_0^{h_0} x dh' = 0 \quad (22)$$

Eqs. (21) and (22) allow $D_s(h)$ to be calculated from an experimentally measured spreading profile.

Fig. 4 shows the diffusion coefficient $D_s(h)$ as a function of film thickness for various molecular weights. $D_s(h)$ reaches a maximum value at a thickness of 1 nm. The height at which $D_s(h)$ has its maximum value is close to the radius of gyration R_g of PFPE-Z. Thereafter, it decreases monotonically and follows a relationship, $D_s(h) \propto 1/h$, for a higher film thickness. These trends are consistent with Eqs. (9) and (10). Therefore, it is assumed that van der Waals interaction is the dominant driving force for PFPE Z on an amorphous carbon surface for film thickness greater than a mono-layer. The results of least squares fitting of experimental data to $D_s(h) = (A/6\pi\eta)[3/(\beta h^2) + 1/h]$ are summarized in Fig. 5. The value of β is nearly constant independent of molecular weight. The molecular weights of our sample are quite small. So we expect that $D_s \propto$

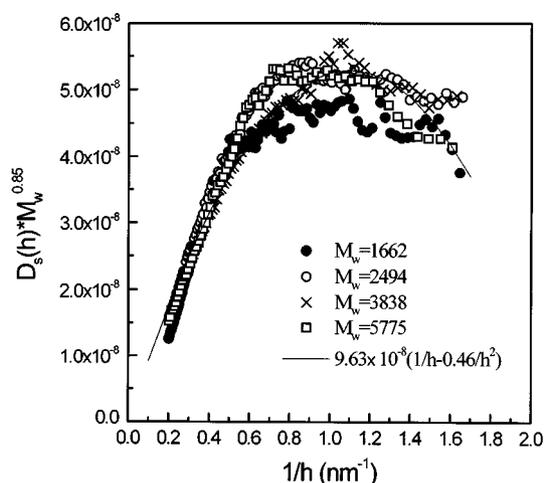


Fig. 5. Comparison between the present analysis with experimental data of Ma [1998] for thick thin-film regime.

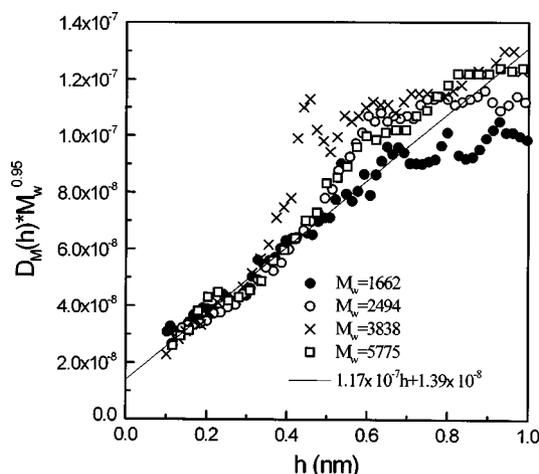


Fig. 6. Comparison between the present analysis with the experimental data of Ma [1998] for thin thin-film regime.

$M_w^{-1.5}$. However, as shown in Fig. 5, $D_s \propto M_w^{-0.85}$ seems to be quite reasonable. From this, we can assume that near the solid surface the molecular conformation is quite different from bulk, so the viscosity near the solid surface is quite different from that of bulk.

For the sub-monolayer regime, $D_s(h)$ increases as the film thickness increases, as shown in Fig. 4. Novotny [1990] suggested that $D_s(h)$ should remain constant; however, Ma's experimental results are inconsistent with his suggestion. Cazabat et al. [1990] discussed the relation between various adsorption-desorption isotherms and surface diffusion coefficients. They show that the surface diffusion coefficient for a sub-monolayer regime is a function of film thickness. We correlate the experimental results based on Eq. (17) in Fig. 6. As shown in this figure, Eq. (17) represents the experimental data, especially for a thinner regime. The slope seems independent of molecular weight for a thinner regime. As the film thickness increases, the experimental data deviate from Eq. (17). Therefore, it seems that the higher order terms should be considered for a thicker regime.

CONCLUSION

The spreading characteristic of PFPE Z was analyzed theoretically. The slip boundary condition instead of the conventional no-slip boundary condition was applied in a thick-thin film regime (hydrodynamic analysis), and this modification explained the experimental results more reasonably. The surface diffusion coefficient had the maximum value at $h \approx 1$ nm and decreased as $D_s \propto 1/h$ for the thicker regime. The two-dimensional virial equation was employed to analyze thin-thin film (sub-monolayer) regime. In thin-thin film regime the surface diffusion coefficient was roughly proportional to film thickness and inversely proportional to molecular weight.

NOMENCLATURE

- A : Hamaker constant
 B : first virial coefficient
 C : second virial coefficient

D_s	: surface diffusion coefficient
F	: free energy
h	: thickness of polymeric film [m]
k	: Boltzmann constant
P	: two-dimensional pressure
q	: volumetric flow rate [m ³ /s]
S	: surface area
T	: temperature [K]
v	: velocity [m/s]
x, z	: horizontal and vertical coordinates [m]

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