

Monte Carlo Simulation of Lubricant Spreading on Nitrogenated and Hydrogenated Carbon Surfaces

Min Chan Kim* and Sang Baek Lee*

질소와 수소를 포함하는 탄소 표면위에서의 윤활제의 퍼짐에 관한 Monte Carlo 모사

김민찬* · 이상백*

ABSTRACT

The spreading profiles of perfluoropolyalkylether (PFPE) lubricants on hydrogenated and nitrogenated carbon surfaces are analyzed by Monte Carlo simulations based on the lattice-gas model (Ising model). We consider lattice structure effects and modified interaction parameters. The simulated results explain the experimental spreading profile of PFPE lubricants on modified carbon surfaces.

Key words : Monte Carlo simulation, lubricant spreading, nitrogenated and hydrogenated carbon surface

I. Introduction

The investigation of the spontaneous spreading of polymeric liquid films on solid surfaces at the microscopic level has gained considerable interest in recent years due to increased scientific importance¹⁾ and disk tribology for application in high-performance disk drive systems²⁾. The spreading properties of perfluoropolyether(PFPE) films, with and without reactive end groups (FomblinTM Zdol and Z, respectively), on various nitrogenated and hydrogenated carbon surfaces were examined. To understand the spreading profiles observed from

micro-ellipsometry (SME) measurements for the above systems, we performed Monte Carlo (MC) simulations. The remarkable observation by Ma *et al.*²⁾ shows that the complex molecular layering structure for PFPE films with reactive end groups was observed, whereas for PFPE films without reactive end groups, no layering was observed.

II. Monte Carlo Simulation

An initial MC simulation was performed by Ma³⁾ to explain the peculiar spreading profiles reported in Ref. 2 by incorporating four different interactions: molecule/molecule, molecule/substrate, end group/end group, and end group/substrate(a molecule is denoted

* 제주대학교 청정화학공학과, 산업기술연구소
Dept. of Chem. Eng. & Res. Inst. Tech., Cheju Nat'l Univ.

as a backbone in the absence of end groups). The essence of the model is based on the lattice-gas model (Ising model), where occupied sites are associated with spin $S=1$ and vacant sites are assigned $S=0$, to explain the spreading properties of Z.

However, end group interaction terms are required to explain the spreading behavior of Zdol and are implemented through the parameter S^z (projection of S in the direction perpendicular to the substrate, z), which is denoted as the direction of spin. S^z identifies the orientation of the end group and was chosen as a slight modification to the Ising model ($S^z = \pm 1$, where a positive value denotes an upward-pointing end group). As a consequence, the system Hamiltonian of simple cubic (SC) lattice may be expressed as:

$$\begin{aligned}
 H = & -\frac{J}{2} \sum_{i,j,k} S_{i,j,k} S_{i-1,j-1,k-1} - A \sum_{i,j,k} \frac{S_{i,j,k}}{k^3} \\
 & - \sum_{i,j,k} \frac{K(k)}{4} (S_{i,j,k}^z + 1)(S_{i,j,k}^z - 1) \\
 & + \sum_{i,j,k} \frac{W(k)}{2} (S_{i,j,k}^z - 1)
 \end{aligned} \quad (1)$$

here k is a counting index normal to the surface. The first two terms in Eq. (1) describe non-reactive molecules (molecule/molecule interaction and molecule/surface interaction). J is the nearest neighbor coupling constant, and A is related to the Hamaker constant originating from van der Waals interactions. The third and fourth terms in Eq. (1) represent end group characteristics (descriptive for reactive end group molecules only), where K and W represent the end group/end group interactions and the end group/substrate interactions, respectively. Therefore, by setting $K = W = 0$, we recover the Hamiltonian for non-reactive molecule systems.

The Metropolis method, where each MC step interrogates all of the molecules, is employed to

simulate spreading characteristics. The movement of an interrogated molecule depends both on whether the project site is empty and if a favorable system energy change is associated with the movement. The probability of movement is $P = 1 / \{1 + \exp(\Delta H / k_B T)\}$, where $\Delta H = H^f - H^i$.

H^i and H^f are the energy of the system before and after a movement is made. k_B and T represent the Boltzmann constant and absolute temperature, respectively. The time step for each cycle is arbitrary.

Even though this treatment oversimplifies physical reality, the original formulation presented by Ma³¹ qualitatively explains the obtained experimental results from SME. We introduced two novel modifications (screening length and change in lattice structure) in addition to the predescribed model given in Reference 3.

Equation (1) unfortunately results in severe evaporation depending on the choice of the interaction parameter, J . To investigate this issue, we systematically tuned interaction parameters and adopted hexagonal close packed (HCP) lattice structures. The introduction of a screening length accounts for the complex surface effects of hydrogenated and nitrogenated surfaces. In Eq. (1),

$K(k)$ and $W(k)$ (*i.e.* K and W vary with distance from the surface) are the coupling parameters between end groups and between end groups and the surface, where $K > 0$ and $W > 0$ imply favorable end group interactions. However, to describe complex surface effects, we introduced the concept of screening length, given by $K(k) = K_0 \exp(-k/d_1)$, where d_1 is the screening length. This modification allows K to exponentially decay with increasing distance from the surface. End group/surface interactions affect the first layer only: that is $W(k) = W_0$ and $W(k) = 0$ otherwise.

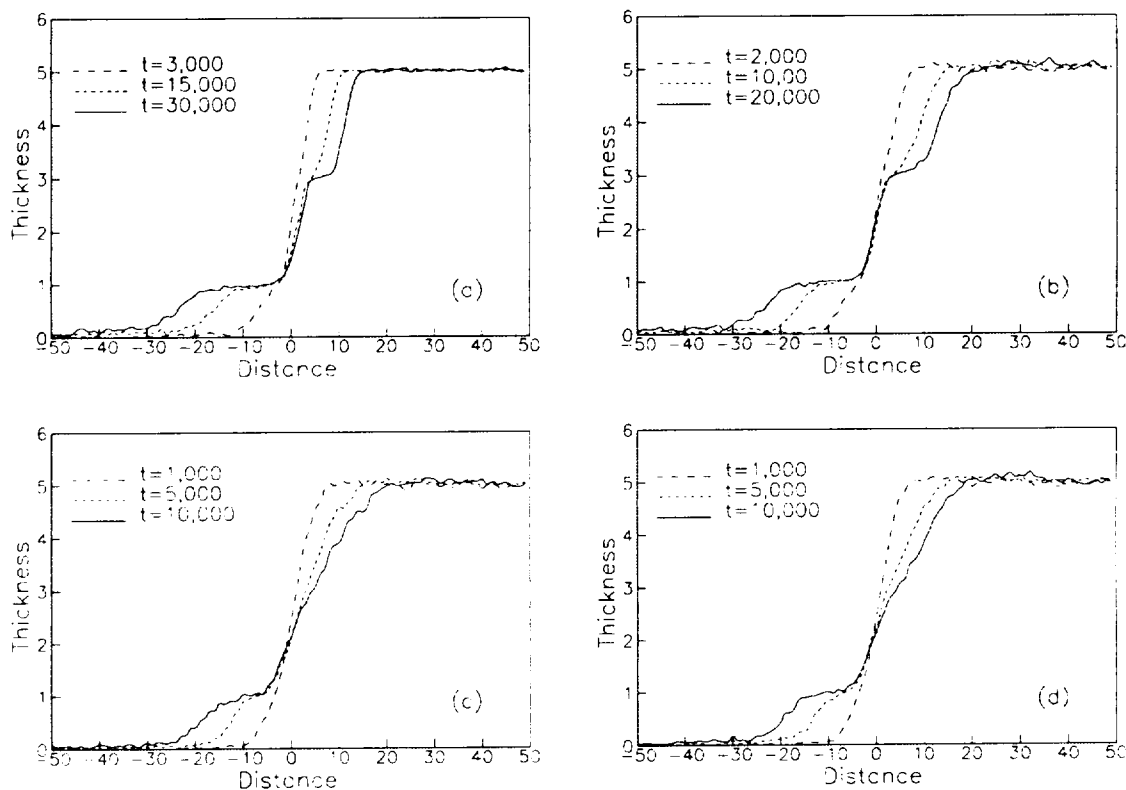


Fig. 1 Simulation results of Zdol with $J=1$, $A=10$, $K_0=3$ (a) $W_0=3$ and $d_1=4$. (b) $W_0=8$ and $d_1=2$. (c) $W_0=3$ and $d_1=4/3$. and (d) $W_0=8$ and $d_1=4/3$ for HCP lattice structure: $t \equiv$ number of time steps.

III. Results and Discussions

A comparison between PFPE Z and PFPE Zdol for the SC lattice case is illustrated in Fig. 1. Case (a) is for the Z and case (b) is for the Zdol with $d_1=4$. A drastic change is apparent between Zdol and Z case: Zdol possesses a layering structure, while Z does not. These results are consistent with experimental observations from Ma *et al.*⁴ However, simulated results show severe oscillation along the top edge due to the evaporation of molecules. To resolve this evaporation problem, we implemented an HCP (instead of SC) lattice structure. The results for a

typical simulation are presented in Fig. 2. As you can see, the evaporation effects are reduced. Interestingly, the case of $d_1=10$ resembles thermally bonded Zdol, and the $d_1=4$ profile is similar to naturally bonded Zdol on a carbon surface.

It should be noted that evaporation effects may also be reduced by increasing the molecule/molecule interaction parameter J . Simulation results without the introduction of the screening length parameter are presented in Fig. 3. When the nitrogenated and hydrogenated carbon surface is considered, it is assumed that the interaction parameter between endgroups has the same value; however, the interaction between surface and end group takes a different form.

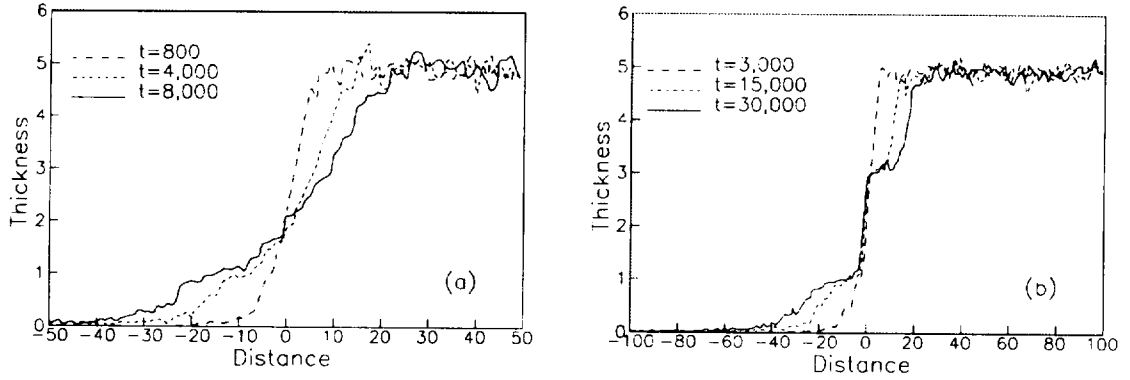


Fig. 2 Simulation results for (a) Z with $J=1$ and $A=10$, and (b) Zdol with $J=1$, $A=10$, $K_0=8$, $W_0=10$, $d_1=4$ for SC lattice structure: $t \equiv$ number of time steps.

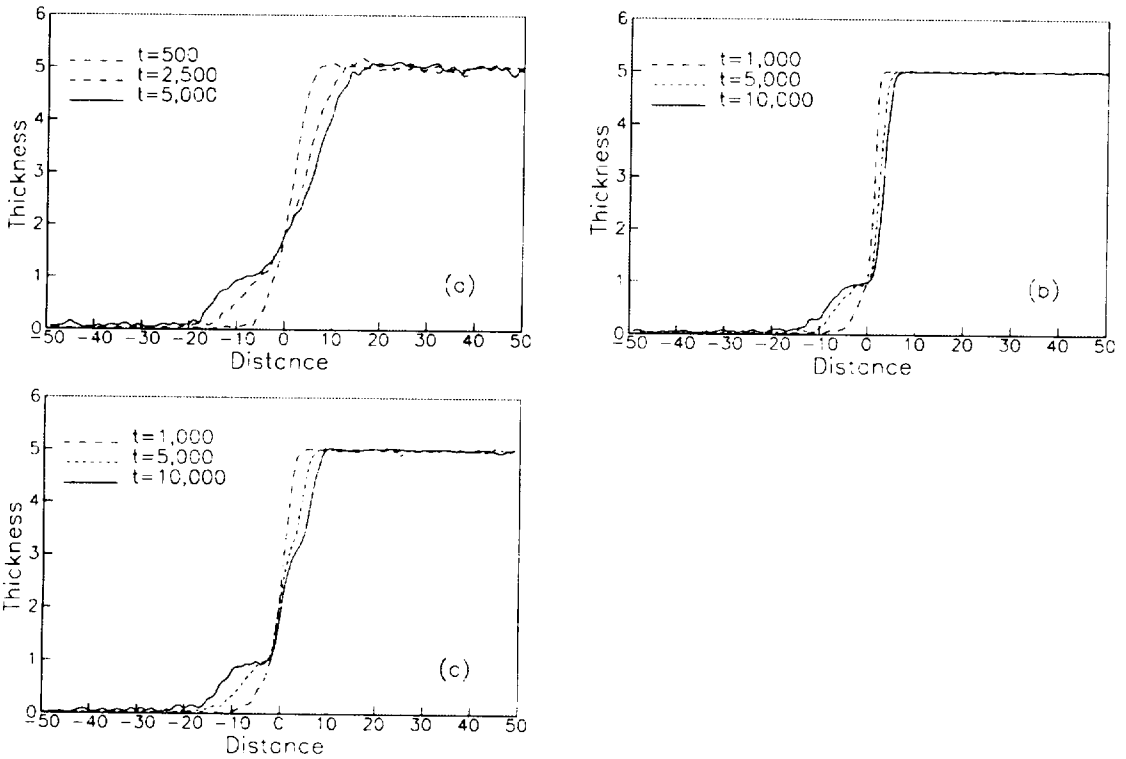


Fig. 3 Simulation results for (a) Z with $J=1$ and $A=10$, (b) Zdol with $J=1$, $A=10$, $K_0=3$, $W_0=10$, $d_1=10$ and (c) Zdol with $J=1$, $A=10$, $K_0=3$, $W_0=10$, $d_1=4$ for HCP lattice structure: $t \equiv$ number of time steps.

Various sets of parameters are considered in our simulation, and some of them are presented in Fig. 4.

The spreading profiles are strongly dependent on d_1 , while W has little effect on the spreading profiles.

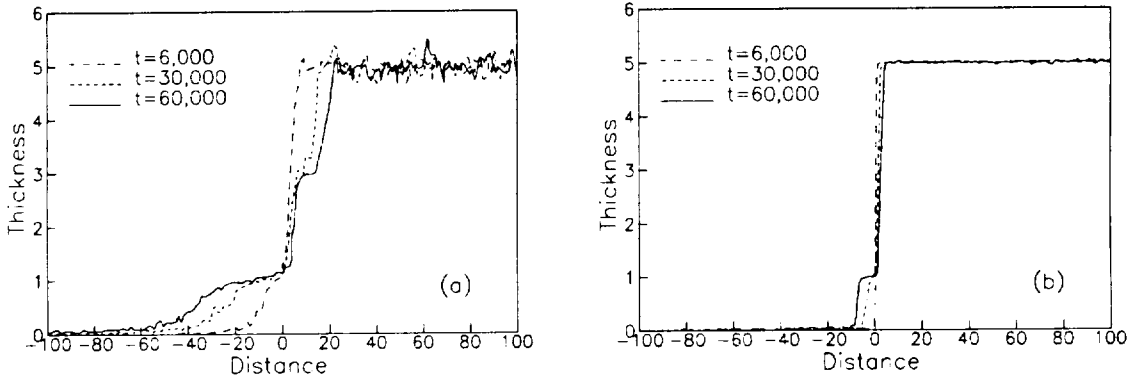


Fig. 4 Simulation results for Zdol with $A = 10$, $K = 4$, and $W = 10$ (a) $J = 1$, and (b) $J = 2$ without introduction of screening length: $t \equiv$ number of time steps

When compared with experimental data for nitrogenated and hydrogenated carbon surfaces, it appears that hydrogen contents decreases d_1 and increase W . However, the nitrogen content decreases both d_1 and W . The effect of nitrogen contents on the screening length is quite strong. The spreading profiles of case (b) and (d) resemble spreading profiles obtained from nitrogenated carbon surfaces with carbon to nitrogen ratios of 10% and 50%, respectively.

IV. Conclusions

For molecules with non-reactive end group (Z), van der Waals forces play a dominant role in the spreading characteristics. However, the surface energy of the molecules with reactive end groups (Zdol), which includes interaction between end groups as well as between end groups and the surface, is a dominant factor. By employing the screening length concept, the layering structure for Zdol is more clearly obtained, and the resulting profiles more reasonably emulate the experimental results. Hydrogen and nitrogen content in carbon surfaces is closely tied to both the end group/surface interaction parameter W and

screening length d_1 . Our results show that evaporation is reduced as the lattice structure becomes more compact.

요약

수소 또는 질소를 포함하는 탄소 표면에서의 perfluoropolyalkylether (PFPE) 윤활제의 퍼짐 현상을 Ising model 형태의 격자 모델을 사용하는 Monte-Carlo 모사를 통하여 해석하였다. 격자 구조의 효과와 변환된 형태의 상호 작용 인자를 고려하였다. 모사된 결과는 개질된 탄소 표면에서의 PFPE 윤활제의 퍼짐에 대한 실험 결과를 잘 설명하여 주었다.

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