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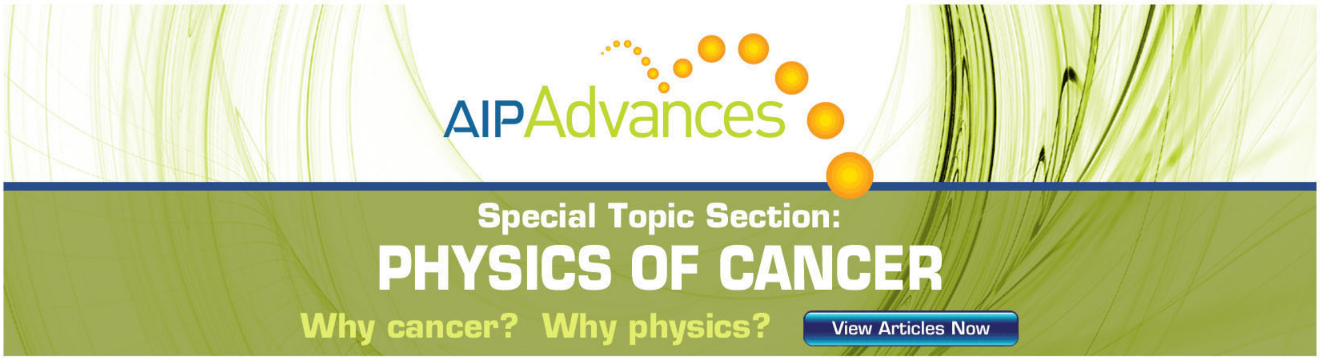

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Simulation of ultrathin lubricant films spreading over various carbon surfaces

Stephen J. Vinay, David M. Phillips, and Young Sil Lee
Department of Chemical Engineering and Data Storage Systems Center, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

Charles M. Schroeder
Department of Chemical Engineering, Stanford University, Stanford, California 94305

Xiaoding Ma
Seagate Recording Media Group, 47010 Kato Road, Fremont, California 94538

Min C. Kim
Department of Chemical Engineering, Cheju National University, Cheju 690-756, Korea

Myung S. Jhon[a]
Department of Chemical Engineering and Data Storage Systems Center, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

The mathematical modeling of the dynamics of ultrathin perfluoropolyalkylether (PFPE) films, taking into consideration both the disk carbon surface composition and lubricant endgroup functionality, is described. Theoretical development based on the Monte Carlo method was employed to emulate experimental spreading data. In this model, we construct a system Hamiltonian based on a lattice-gas model by explicitly incorporating four classes of interactions: molecule/molecule, molecule/surface, endgroup/endgroup, and endgroup/surface, where a molecule is denoted as a backbone in the absence of endgroups. Spreading properties are investigated by tuning the lubricant interactions to model PFPE Z (without polar endgroups) and PFPE Zdol (with polar endgroups) on several surfaces. The simulations qualitatively describe the spreading profiles for molecules with and without polar endgroups. Acquired from *N*-frame animations, L-t plots are constructed and provide a qualitative comparison with the experimental data obtained from scanning microellipsometry. © *2000 American Institute of Physics.* [S0021-8979(00)39408-7]

INTRODUCTION

The role of the lubricant in hard disk drive (HDD) systems is becoming critically important to reliability as a result of decreased head fly height, driven by the demand for increased recording density. Typically, only a 2 nm thick lubricant film protects the disk surface from mechanical and thermal damage during intermittent contact between the head and disk.

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 both its increased scientific importance and its application to high-performance HDD systems.[1,2] The spreading properties of perfluoropolyalkylether (PFPE) films, with and without polar endgroups (Fomblin™ Zdol and Z, respectively), on various nitrogeneted and hydrogenated carbon surfaces were examined.[3] The chemical structure of PFPE is

$$\text{X-CF}_2 \text{+}(\text{OCF}_2\text{-CF}_2)_p\text{-}(\text{OCF}_2)_q\text{+}\text{OCF}_2\text{-X} \quad (p/q \approx 2/3),$$

where X denotes an endgroup, and $X \equiv F$ for Z and $X \equiv CH_2OH$ for Zdol.

To describe the experimental spreading profiles observed from scanning microellipsometry (SME) measurements, we developed Monte Carlo (MC) simulations based on the lattice-gas (Ising) model. Simulation results are qualitatively similar to the remarkable experimental observations by O'Connor *et al.*[1] and Ma *et al.*,[2] which illustrate a complex molecular layering structure for PFPE films with polar endgroups, whereas no layering structure was observed for PFPE films without polar endgroups.

MONTE CARLO SIMULATION

MC simulations were first performed by Ma *et al.*[4] to describe the peculiar spreading profiles of PFPEs on amorphous carbon surfaces by incorporating four different interactions: molecule/molecule, molecule/surface, endgroup/endgroup, and endgroup/surface where a molecule is denoted as a backbone in the absence of polar endgroups. All of these interactions are short range (nearest neighbor only), with the exception of the molecule/surface interaction, which decays in a manner similar to a van der Waals interaction. Molecules are approximated as reactive spheres, where an occupied lattice site is assigned a spin $S=1$ (a vacant site is assigned $S=0$). By excluding all endgroup interactions, simulations qualitatively describe the spreading properties of Z.

Endgroup interaction terms are required to explain the spreading behavior of molecules with polar endgroups (Zdol) and are implemented through the spin parameter S^Z, which identifies the orientation of a polar endgroup ($S^Z = \pm 1$,

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[a] Electronic mail: mj3a@andrew.cmu.edu

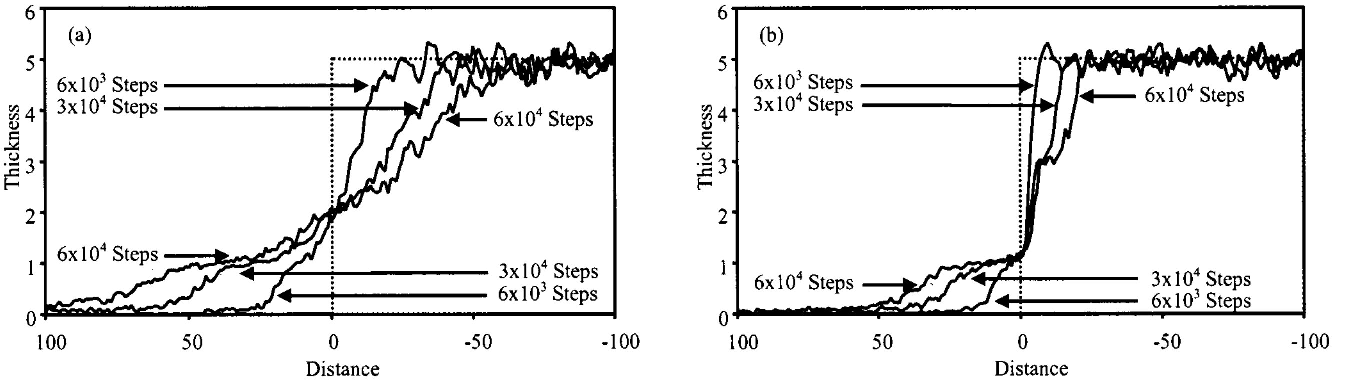

FIG. 1. Simulated spreading profiles for (a) PFPE Z and (b) Zdol ($K_0/k_BT=4$, $W_1/k_BT=10$, $d\rightarrow\infty$). $J/k_BT=1$ and $A/k_BT=10$.

where a positive value denotes an upward-pointing endgroup). As a consequence, the system Hamiltonian H for a simple cubic lattice may be expressed as

$$H=-\frac{J}{2}\sum_{i,j,k} S_{i,j,k}S_{i\pm1,j\pm1,k\pm1}-A\sum_{i,j,k}\frac{S_{i,j,k}}{k^3}$$
$$+\sum_{i,j,k}\frac{K(k,d)}{4}(S^Z_{i,j,k}+1)(S^Z_{i,j,k+1}-1)S_{i,j,k}S_{i,j,k+1}$$
$$+\sum_{i,j,k}\frac{W(k)}{2}(S^Z_{i,j,k}-1)S_{i,j,k}, \quad (1)$$

where k is a counting index normal to the surface. The first two terms in Eq. (1) adequately describe molecules with nonpolar endgroups (Z). J is the nearest neighbor, molecule/molecule coupling constant, and A is the molecule/surface coupling constant, which is related to the Hamaker constant originating from van der Waals interactions. The third and fourth terms in Eq. (1) represent endgroup characteristics, necessary for molecules with polar endgroups only; $K(k,d)$ and $W(k)$ are the endgroup/endgroup and the endgroup/surface coupling constants, respectively. We have generalized the Hamiltonian constructed by Ma *et al.* by incorporating k dependency into the polar end-group interaction parameters $K(k,d)$ and $W(k)$, where the parameter d is a screening length, which is assumed to affect only the endgroup/endgroup interaction strength. In Eq. (1), $K(k,d)>0$ and $W(k)>0$ imply favorable endgroup interactions. Therefore, by setting $K(k,d)=W(k)=0$, we recover the Hamiltonian for PFPEs with nonpolar endgroups.

Each MC step randomly interrogates every molecule exactly one time. The movement of an interrogated molecule depends both on whether the projected site is empty and if a favorable system energy change is associated with the movement. The probability of movement P into a vacant site is

$$P=\{1+\exp(\Delta H/k_BT)\}^{-1}, \quad (2)$$

where $\Delta H\equiv H^f-H^i$ (H^i and H^f are the initial and final system Hamiltonians for a movement). Here, k_B and T represent the Boltzmann constant and absolute temperature, respectively.

The original simulations presented by Ma *et al.*[4] qualitatively explain experimental spreading results over an amorphous carbon surface obtained from SME. However, to describe spreading on hydrogenated and nitrogenated carbon surfaces, we introduced a d dependence:

$$K(k,d)=K_0\exp(-k/d), \quad (3)$$

thus implying a transition from surface behavior to bulk behavior. $W(k)$ for our simulations is defined as

$$W(k)=W_1\delta_{1,k}, \quad (4)$$

where $\delta_{1,k}$ is the Kronecker delta.

RESULTS AND DISCUSSION

A comparison between simulation results for molecules with nonpolar (Z) and polar (Zdol) endgroups is illustrated in Fig. 1. A dramatic difference is apparent between Figs. 1(a) and 1(b): the Z profile is relatively smooth and spreads more rapidly, whereas the Zdol profile possesses a complex layered structure. These results are consistent with the experimental observations by Ma *et al.*,[4] which showed that molecules with polar endgroups demonstrate a first layer that is one molecule thick (the thickness of the first layer is on the order of the radius of gyration of the PFPE in the bulk), with subsequent layers approximately twice the thickness of the first. Also, Z with nonpolar endgroups spreads more rapidly than Zdol with its polar endgroups and layered profile.

A simulation result with a screening length $d=4$ is presented in Fig. 2 and shows a strong dependence on the

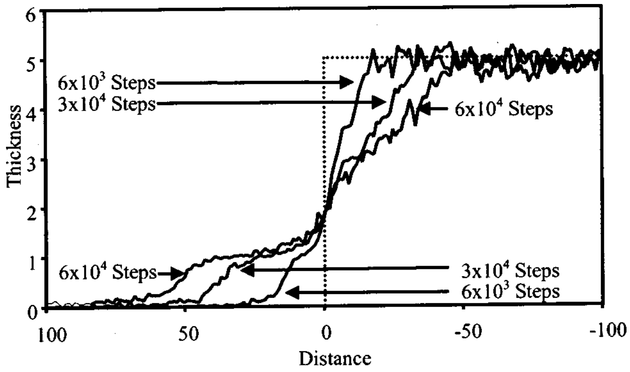

FIG. 2. Simulated spreading profile for Zdol with a finite screening length ($J/k_BT=1$, $A/k_BT=10$, $K_0/k_BT=4$, $W_1/k_BT=10$, $d=4$).

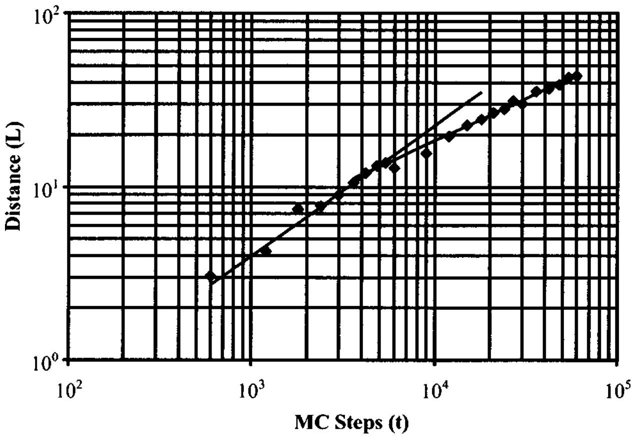

FIG. 3. *L*-*t* plot (Zdol) for a 5% isoheight ($J/k_BT=1$, $A/k_BT=10$, $K_0/k_BT=4$, $W_1/k_BT=10$, $d\to\infty$).

screening length *d*. Comparing Fig. 1(b) [where $d\to\infty$, implying $K(k,d)=K_0$ in Eq. (3)] and Fig. 2, the complex layered structure relaxed with a decreasing screening length, indicated by a decrease in steepness of the layering in the ''shoulder'' area. This behavior is qualitatively similar to experimental spreading data on hydrogenated and nitrogenated carbon surfaces; it appears that the hydrogen or nitrogen content decreases the screening length *d*. Figure 2 resembles SME spreading profiles obtained from hydrogenated carbon surfaces with a hydrogen-to-carbon ratio of 50%.

An alternative way to present the simulated spreading behavior is shown in Fig. 3 for Zdol. This *L*-*t* plot was constructed by plotting the distance that an isoheight (a region of constant thickness that changes position with time) in the spreading profile travels from the initial sharp boundary versus the number of MC steps. The isoheight chosen was 5% of the initial five-molecule-thick profile, and the simulated *L*-*t* response shows a distinct transition between short and long times. This is qualitatively similar to the experimental *L*-*t* behavior presented by O'Connor *et al.*[1] The long-term behavior shows $L\propto t^{1/2}$, thus satisfying the criteria for the surface diffusion assumption,[1,2] however, the short-term behavior shows spreading that is markedly faster than $L\propto t^{1/2}$.

Recently we have animated the resulting simulation data to visualize PFPE molecular dynamics. Preliminary results demonstrate layer formation for molecules with polar endgroups. We are currently simulating surface energy profiles[5] using the method described here. By altering $K(k,d)$ and $W(k)$, we intend to examine the transition from ''steep'' to ''mild'' (or no) shouldering in the spreading profiles. Future work will include animating the paths of individual molecules and polar endgroup orientations to gain further insight into molecular layer formation.

CONCLUSIONS

For molecules with polar endgroups (Zdol), endgroup coupling, which includes interaction between polar endgroups as well as between endgroups and the surface, plays a dominant role in the dynamic behavior of the PFPE film. By employing the screening length concept, a layered structure similar to Zdol spreading on hydrogenated and nitrogenated carbon surfaces is emulated. The effect of hydrogen and nitrogen content in the carbon surface is closely tied to both $W(k)$ and *d* in our simulations. A qualitative agreement between simulated and experimental *L*-*t* behavior is established, thus demonstrating transition behavior and providing criteria for the surface diffusion assumption.

ACKNOWLEDGMENT

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