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STUART A. RICE

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STUART A. RICE

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CONTRIBUTORS

A. I. BURSHTEIN, Department of Chemical Physics, The Weizmann Institute of Science, Rehovot 76100, Israel

MYUNG S. JHON, Department of Chemical Engineering and Data Storage Systems Center, Carnegie Mellon University, Pittsburgh, PA 15213-3890, U.S.A.

UDAYAN MOHANTY, Eugene F Merkert Chemistry Center, Department of Chemistry, Boston College, Chestnut Hill, MA 02467, U.S.A.

YURIY L. RAIKHER, Institute of Continuous Media Mechanics, Ural Branch of RAS, 1 Korolyev Street, Perm 614013, Russia

VICTOR I. STEPANOV, Institute of Continuous Media Mechanics, Ural Branch of RAS, 1 Korolyev Street, Perm 614013, Russia

INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field that we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

Stuart A. Rice

CONTENTS

PHYSICOCHEMICAL PROPERTIES OF NANOSTRUCTURED PERFLUOROPOLYETHER FILMS

MYUNG S. JHON

Department of Chemical Engineering and Data Storage Systems Center, Carnegie Mellon University, Pittsburgh, Pennsylvania, U.S.A.

CONTENTS

This chapter presents fundamental scientific tools as well as potential applications relevant to the emerging field of nanotechnology. In particular, understanding the behavior of molecularly thin lubricant films is essential for achieving durability and reliability in nanoscale devices, and the experimentation and theory for the physicochemical properties of ultrathin perfluoropolyether (PFPE) films are reviewed. A method for extracting spreading properties from the scanning microellipsometry (SME) for various PFPE/solid surface pairs and the rheological characterization of PFPEs are examined at length. The

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interrelationships among SME spreading profiles, surface energy, rheology, and tribology, are discussed as well. Phenomenological theories, including stability analysis and microscale mass transfer, are introduced to interpret ultrathin PFPE film nanostructures qualitatively. In addition, rigorous simulation tools, including a lattice-based simple reactive sphere model, the off-lattice bead-spring Monte Carlo method, and molecular dynamics method, are examined. These tools may accurately describe the static and dynamic behaviors of PFPE films consistent with experimental findings and thus will be suitable for describing the fundamental mechanisms of film dewetting and rupture due to instability arising from nanoscale temperature and pressure inhomogeneities. Nanotribological applications, such as finding an optimal disk lubricant based on a molecule-level interaction of the lubricant with solid surfaces, will be explored.

I. INTRODUCTION

Nanoscale confined polymers are important for their potential industrial applications. The functionalities of polymer chain and solid surfaces are key control factors in determining the material designs for these applications. A fluid confined in a nanoscale system will dramatically alter its structural and dynamic properties. Because of broad technological interest, numerous studies on nanoscale confined fluids have been investigated, both theoretically and experimentally by scientists and engineers from a variety of backgrounds, including data storage, synthetic catalysis, polymer synthesis and physics, tribology, robotics, and medicine [1]. The behavior of materials having constituents with dimensions on the nanometer scale is remarkably different from the behavior in bulk state, which has led to a new paradigm that we now refer to as *nanotechnology.*

Molecularly thin lubricant film is an important application of nanoscale confined polymeric fluids, and is the focus of this chapter. Ultrathin lubricant films are necessary in high-density data storage to increase the reliability and performance of hard-disk drive (HDD) systems [2–4]. Spinoff and intermittent contact between the slider (or head) and the lubricated disk [ultrathin perfluoropolyether (PFPE) films are applied to the disk's carbon-overcoated surface, as shown in Fig. 1.1] cause loss and reflow of the lubricant film. The relevant HDD technology is summarized briefly in the end-of-chapter Appendix Section A.I, which provides an overview of how certain information technology devices are controlled by nanoscale chemistry.

The lubricant dynamics can alter the nanoscale aerodynamics of the slider. Conversely, the lubricant morphology and dynamics may be altered because of the presence of the slider. For these types of applications, a molecule-level understanding of the lubricant interaction with nanoscale airbearing and solid surfaces is critical. The HDD industry must cope with problems of lubricant film uniformity, roughness [5], durability [6], and stability [7] in order to achieve its goal of increasing areal density.

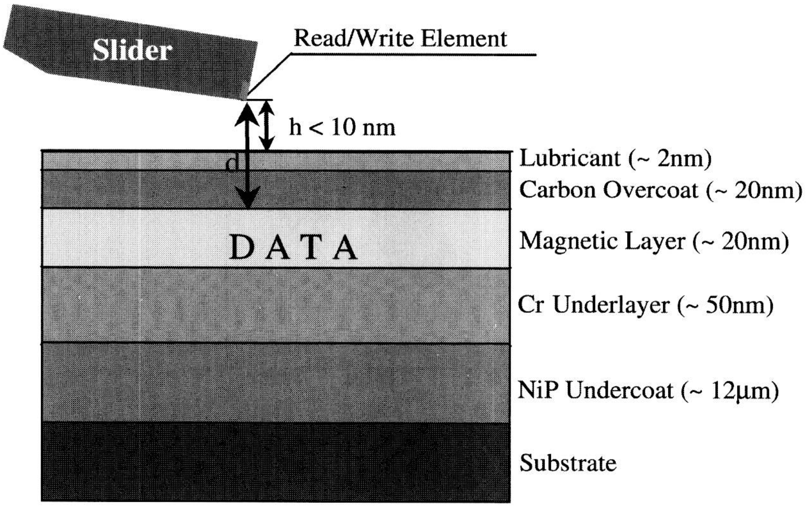


Figure 1.1. Configuration of the head–disk interface in HDD [see Fig. 1.4(*a*)].

The commercially available PFPE Z and Zdol (Montedison Co. [8] products) are random copolymers with the linear backbone chain structure

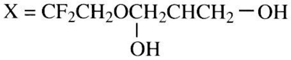
$$X\text{—}[(OCF_2\text{—}CF_2)_p\text{—}(OCF_2)_q]\text{—}X \quad \left(p/q \cong \tfrac{2}{3}\right)$$

where X (endgroup) is CF_3 in PFPE Z and CF_2CH_2OH in PFPE Zdol. Note that Zdol has hydroxyl groups at both chain ends, which exhibit moderate interactions with solid surfaces, e.g., silica and carbon.

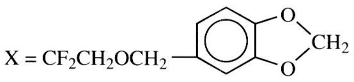
In addition, we examined PFPE ZdolTX [9] with "bulky" endgroups as a potential lubricant, which is shown below:

$$X = CF_2CH_2\text{—}(OCH_2CH_2)_{1.5}\text{—}OH$$

The structures of PFPE Z, Zdol, and ZdolTX are shown in Figure 1.2. Other PFPEs that have been investigated [10] include Ztetraol and AM2001; Xs are as follows:

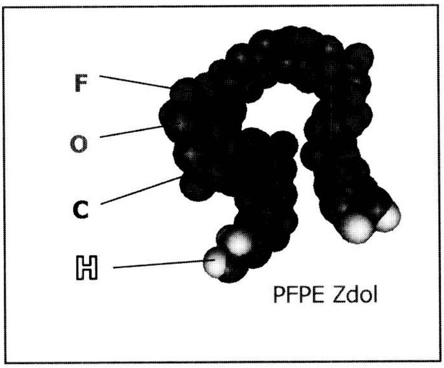
Ztetraol:


$$X = CF_2CH_2OCH_2\underset{\substack{|\\ OH}}{CH}CH_2-OH$$

AM2001:


The use of additives, such as X1-P, may enhance the reliability of an HDD [11].

(*a*)



(*b*)

	Molecular Structure	**PFPE/Solid Interaction**	**Backbone** $(OCF_2—CF_2)_p—(OCF_2)_q$ **End Group**
Z		weak	CF_3
Zdol		moderate	CF_2CH_2OH
ZdolTX		strong	$CF_2CH_2 - (OCH_2\,CH_2)_{15}–OH$

Figure 1.2. (*a*) Molecular structure of PFPEs; (*b*) simplified view of (*a*); the larger circles indicate stronger endgroup interactions with the solid surface.

Scientists and engineers working in the information storage industries (e.g., Seagate, Hitachi, and Maxtor) have conducted numerous studies on PFPEs and their thin-film properties. Several academic institutions in the United States [University of California (Berkeley, Computer Mechanics Laboratory; San Diego, Center for Magnetic Recording Research), Ohio State University (Computer Microtribology and Contamination Laboratory), and Carnegie Mellon University (Data Storage Systems Center)] have been actively investigating the role of lubricants and their applications to data storage

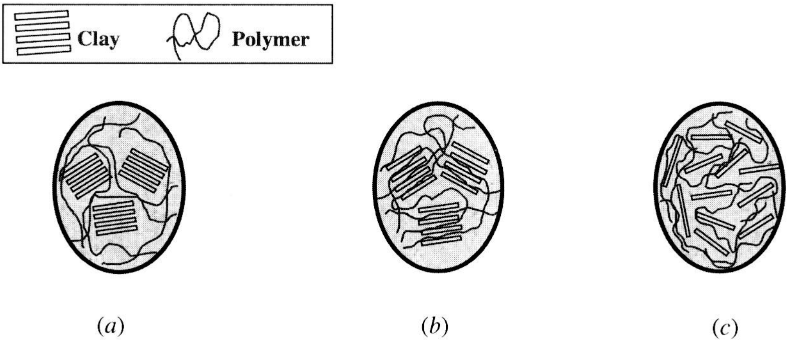


Figure 1.3. The microstructure of clay dispersed in the polymer matrix: (*a*) conventional composite; (*b*) extended polymer chains intercalated between the silicate layers, resulting in a well-ordered multilayer with alternation polymer/inorganic layers, and (*c*) silicate layers (1 nm thickness) exfoliated and dispersed in a continuous polymer matrix.

systems. The Data Storage Institute in Singapore, the largest such institute outside the United States, is involved in nanotribology research relevant to data storage as well. However, despite the plethora of research topics, we will focus only on fundamental scientific issues and our own findings regarding to data storage applications in this review. We will discuss the details of the PFPE experiments, qualitative analysis, and full-scale simulation. Although we will concentrate on selected highlights from our research, other topics will be touched on briefly.

Although not discussed in detail in this chapter, the scientific tools we explored and developed may be applicable to other areas of nanotechnology, such as nanocomposites. The nanocomposites have emerged as a new class of materials during the 1990s. For example, confined polymers solidify at temperatures well above the glass transition temperature as the intercalation rate slows down due to the increased affinity between the polymers and inorganic plate surface. It has been suggested [12] that the timescale of the intercalation process is relatively insensitive to the molecular weight of the polymer when compared to the diffusion coefficient in the confined slit. Various types of nanocomposites have been synthesized and characterized by our research group [13–20]. In addition to the well-known conventional composite (blend system), these nanocomposites can be classified into two distinct structures: intercalated and exfoliated (Fig. 1.3). Specific interactions through modified functional groups on polymer chains, tethered surface modifiers, and silicate surfaces play important roles in determining the molecular architecture for nanocomposites.

Using a variety of commercial and well-characterized polymers, intercalation has led to a wide variety of nanophase hybrids, many of which had not been previously synthesized using the traditional intercalation approaches. The

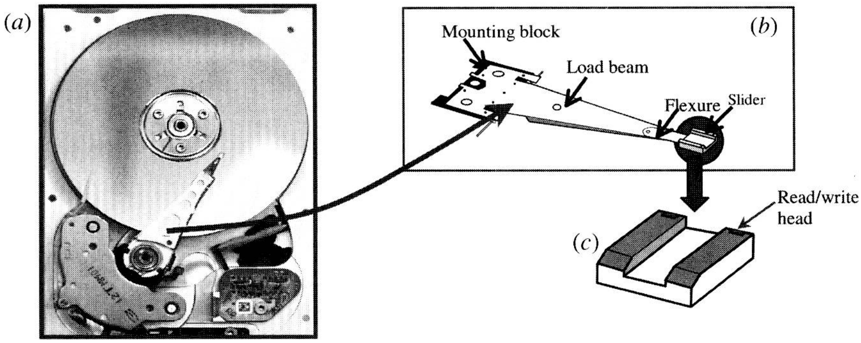
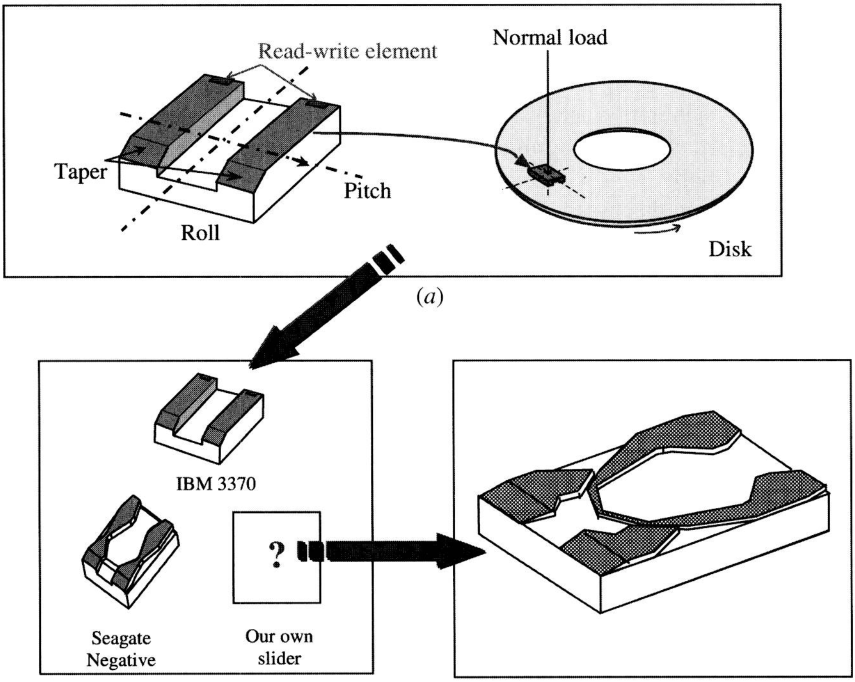


Figure 1.4. (*a*) HDD system; (*b*) schematic of suspension–slider assembly; (*c*) IBM 3370 slider.



(*a*)

(*b*)

Figure 1.5. (*a*) Attitude and (*b*) shape of the slider.

intercalated nanocomposites are composed of macromolecules that are confined on a lengthscale that is small in comparison to the unperturbed molecular dimensions in a bulk state [21]. The energetic cost of perturbing chains is compensated by the topological "entanglement" constraints imposed on the chains.

Thermal and mechanical properties have been drastically improved by nanocomposites [12–33] dispersed with inorganic clays in a polymer matrix, which is characterized by nanometer lengthscale domains. These nanocomposite systems can be similarly examined by the methodology reported in this chapter.

Section A.1 of the Appendix discusses the background for the hard-disk drive (see also Figs. 1.4 and 1.5).

II. EXPERIMENTATION AND QUALITATIVE ANALYSIS

In this section, we will study spreading profiles measured from scanning microellipsometry (SME) and its relationship to various experiments, especially rheology, surface energy, and tribology. Phenomenological theory will be developed to interpret the various experiments as well as interrelation among experiments. Rheology of polymer melts and solutions and stability analysis based on thermodynamics will be studied at length as well.

Section A.2 of the Appendix discusses calculation of the film-thickness-dependent diffusion coefficient from a hydrodynamic model.

A. Scanning Microellipsometry

Figure 1.2 illustrates the various PFPEs. To demonstrate the essence of the spreading phenomena, we examined the "thought experiments" for different lubricant–surface and lubricant–lubricant interactions. This is sketched in Figure 1.6. O'Connor et al. [10,47,48] were the first to systematically carry out spreading experiments using SME to monitor monodisperse PFPE films on silica as they spread with time. Later, Ma et al. [49–52] reproduced and carefully examined these results for various carbon surfaces. Novotny [53], in actuality, pioneered the investigation of PFPEs, although his work mainly dealt with polydisperse PFPE samples. Our coworkers [10,47–52] carefully examined and extended the earlier work of Novotny by investigating the spreading of monodisperse PFPEs ($M_w/M_n < 1.1$, where, M_n and M_w are number average and weight average molecular weight, respectively) on silica and various carbon surfaces in a controlled temperature and humidity environment.

In the experiments of O'Connor et al. [10,47,48], monodisperse fractions of Z and Zdol, which were fractionated via supercritical fluid extraction in CO_2, were dip-coated onto the surface of silicon wafers. Film thickness was controlled

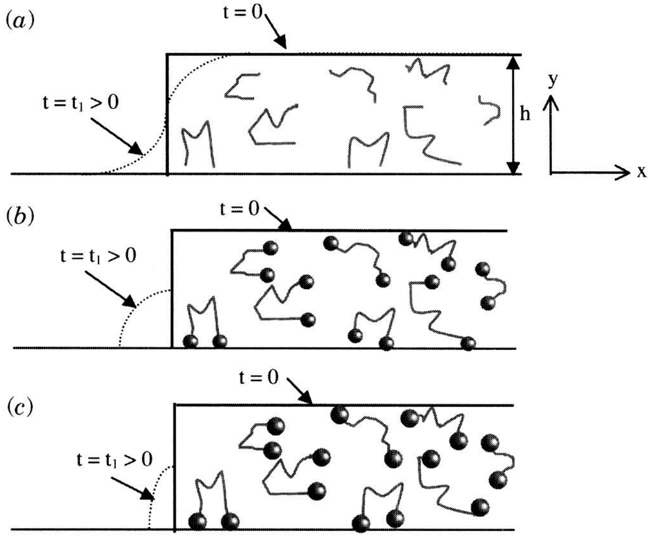


Figure 1.6. Sketch of the spreading profiles from SME as time progresses ($t = 0$ to t_1): (*a*) Z, (*b*) Zdol, and (*c*) ZdolTX. The coordinate system is drawn in (*a*).

by altering the PFPE concentration and draw rate as shown in Figure 1.7. For example, a draw rate of 6 mm/s with a PFPE concentration of 2 g/L generated a 50-Å thin film. An SME apparatus (its components are shown in Fig. 1.8) was used to measure the thickness of the film as it spread with time. The coated wafer was placed on a pedestal-like plate, housed in an environmental chamber with slits for passage of the incident and reflected beams. The chamber was mounted on a stage, which translated the sample across the beam area, and the thickness profile measurements were performed under a controlled temperature and humidity environment. The spreading profile obtained from SME is highly dependent on the PFPE–surface interactions, and provides a fingerprint for each pairing.

Typical SME thickness profiles for monodisperse Z and Zdol, as analyzed by O'Connor et al., are shown in Figures 1.9(*a*) and 1.9(*b*). As the film spreads with time, the spreading front travels along the surface of the silicon wafers. A sharp "spike" for the Z profile in Figure 1.9(*a*) was observed to decay over time. The spreading of Zdol exhibits a characteristic shoulder with a height on the order of the radius of gyration for the PFPE molecules, and the PFPE molecules separate from the initial film layer at a sharp boundary. In addition, Zdol appears to experience partial "dewetting" as indicated by the rough appearance of the SME scan beyond 2 mm [Fig. 1.9(*b*)]. This dewetting phenomenon (investigated

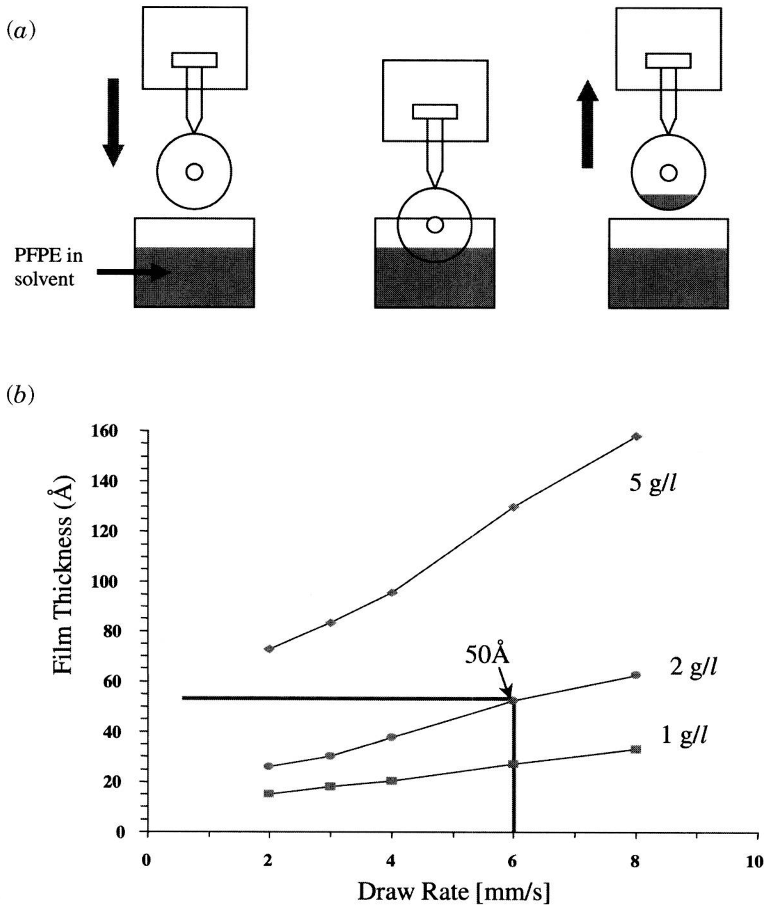


Figure 1.7. (*a*) Partial dip coating of a disk in a PFPE solution; (*b*) film thickness was determined from the PFPE concentration and draw rate.

for "mogul" dynamics [54,55] of nanoscale thin lubricant films) could become very important for airbearing design [40–44,56–59].

Similarly, Figures 1.10(*a*) and 1.10(*b*) represent Z and Zdol spreading experiments on amorphous carbon disks performed by Ma et al. [49–52] a few years after the observations made by O'Connor et al. Again, the Z front (unlike O'Connor et al. [10,47,48], they used polydisperse sample) traveled along the surface, gradually decreasing in height, and the Zdol profile showed a characteristic shoulder or layering structure. However, mass buildup for Z was