

Understanding and utilizing molecular constraints in nanoscale material designs

Scott Sills^{1*} and René M. Overney²

¹Micron Technology Inc., 8000 S. Federal Way, Boise, ID 83707

²Chemical Engineering, University of Washington, Seattle, WA 98195

ABSTRACT

Challenges regarding nanoscale material designs often arise from the collision of two sets of critical length-scales; namely, device dimensions approach the length scale of molecular-level processes. On one hand, these finite size constraints cannot be fully described with quantum or molecular theories; on the other hand, continuum theories characteristic of *top-down design*, breakdown. We are caught in the meso-scale, where characterizing the ensemble-average behavior of a nanoscopic system is both an experimental and theoretical challenge. The work presented here highlights scanning probe microscopy (SPM) techniques used to access the energetic signatures and characteristic length scales for molecular relaxation. The *real-space* information provides insight to the effect of nanoscopic constraints, both internal (chemical, structural) and external (dimensional, interfacial), on the resulting material properties. The technological challenge of utilizing constraints as design opportunities is illustrated with the development of nano-electromechanical systems (NEMS).

Keywords: molecular constraints, atomic force microscopy

1. INTRODUCTION

Molecules are designed to perform certain transport or structure oriented tasks, often in sequence with other molecular tasks, for example, in self-assembled systems. The product of the *directed* molecular teamwork is what drives the idea of *bottom-up design*. The macromolecular systems that perform these tasks exhibit properties rooted in underlying molecular behaviors. The way molecules move, or relax, is governed by a complex potential landscape, which is augmented by dimensional constraints when systems are reduced to the sub-100 nm scale. Consequently, a system's *apparent* properties may shift relative to the bulk, and information derived from traditional bulk-sampling techniques is not always representative of nanoscopic systems. Accurate characterization demands *real-space, in-situ* molecular sensitivity.

In this article, we explore molecular constraints with quantitative scanning probe microscopy (SPM) techniques. Particular emphasis is given to locally probing the interplay between *internal* and *external* constraints, and their effect on material and transport properties in polymer thin-films. The impact on current nano-technological developments is illustrated with the example of terabit data-storage in a nano-electromechanical system (NEMS).^{1,2}

* corresponding author: ssills@micron.com

2. CHARACTERIZATION METHODS

Over several decades, many experimental techniques have evolved for investigating molecular relaxation. Several examples include: multidimensional NMR,³ near-edge X-ray absorption fine structure spectroscopy,⁴ x-ray diffraction,⁵ slow-positron-annihilation spectroscopy,^{6,7} brillouin light scattering,^{8,9} dynamic light scattering,¹⁰ photon correlation spectroscopy and quartz crystal microbalance,¹¹ photobleaching,¹² dielectric spectroscopy,¹³ spectroscopic ellipsometry,¹⁴ & attenuated total reflection.¹⁵ In general, these techniques characterize bulk samples.

Compared to most spectroscopic and scattering techniques, SPM techniques benefit from the molecular sensitivity of a nanoscopic probe. The SPM can be operated with various approaches to probing nano-space. Two techniques for studying polymer relaxation dynamics in *small* systems are friction force microscopy (FFM) and shear modulated force microscopy (SM-FM).¹⁶

2.1 Friction force microscopy (FFM)

FFM simulates a single asperity provided by an ultra-sharp tip on a soft cantilever, Fig. 1. The small contact area, on the order of the molecular dimensions, is insufficient to confine macromolecules and generally allows discussing friction results in terms of thermodynamic equilibrium. The lateral (friction) force, F_L , is measured through the hysteresis in the torsional bending Δx of the cantilever between forward and reverse scans.¹⁷

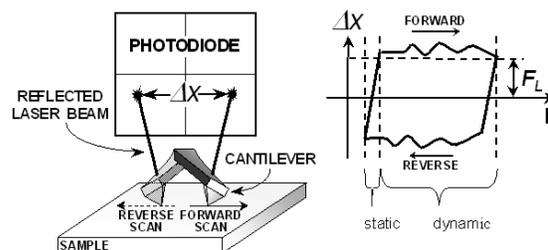


Fig. 1: Working Principle of friction force microscopy (FFM)

The origin for frictional dissipation in polymers has been questioned for 50 years. Since Grosch¹⁸ and Ludema and Tabor,¹⁹ a molecular length-scale has been accessible in friction experiments. However, due to the macroscopic nature of these early investigations, molecular relaxation could only be suspected as a mechanism for dissipation.^{18,19}

FFM has the sensitivity needed to quantify the energetic and dynamic characteristics of the varied relaxation modes

through which energy is dissipated. While this has led to important developments in tribology,²⁰ it offers insight into the molecular-level processes that dictate material behavior in nanoscopic systems. For example, thermo-kinetic FFM studies²¹⁻²³ reveal the energetic barriers for side-chain and backbone relaxations in polymers, illustrated in Fig. 2.

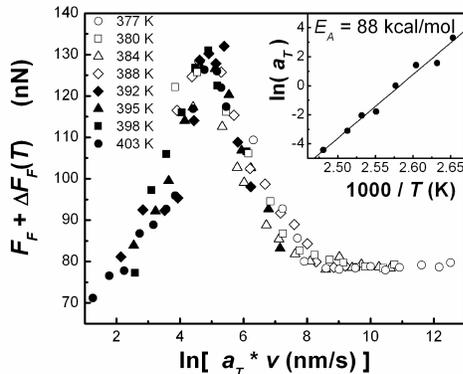


Fig. 2: Superposition of FFM friction (F_F) - velocity (v) isotherms for a polystyrene melt reveals (inset) the energy barrier (E_A) for segmental relaxation in the Arrhenius behavior of the thermal factor (a_T).²³

In polymer melts, nanoscopic friction reveals a highly cooperative dissipation phenomena,²³ known as the *heterogeneous dynamics* of glass formers. It introduces a critical length scale, over which collective molecular motion occurs, i.e. the size ξ_α of a *cooperatively rearranging region* (CRR). FFM dissipation lengths X_d for polystyrene in Fig. 3, support predictions that ξ_α ranges from a collection of monomeric segments to tens of nanometers, involving several molecules.

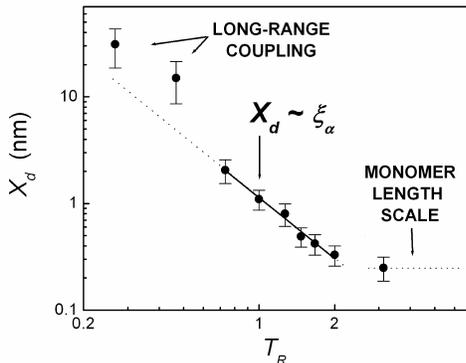


Fig. 3: Frictional dissipation through polystyrene backbone relaxation occurs over a length, X_d , which ranges from monomeric segments to tens of nanometers, involving several molecules. T_R is the reduced temperature, with the onset of the dynamic glass transition at $T_R \sim 1$.²³

The large size of the CRRs approaches that of many nanotechnological devices, which will drive our discussion in Section 3 toward the interactions of molecular systems with their boundaries.

2.2 Shear modulation force microscopy (SM-FM)

SM-FM is a non-scanning compliment to FFM, where material-specific information is inferred from the elastic (or

dissipative) nature of the probing contact. SM-FM involves a nanometer-sharp tip that contacts a sample with a constant normal load, as seen in Fig. 4. The tip is laterally modulated with a nanometer amplitude, Δx_i , that avoids any tip-sample slipping. Using lock-in techniques, the modulation response, Δx_R , is a measure of the contact stiffness, k_{tot} , which contains the sample's elastic modulus.¹⁶

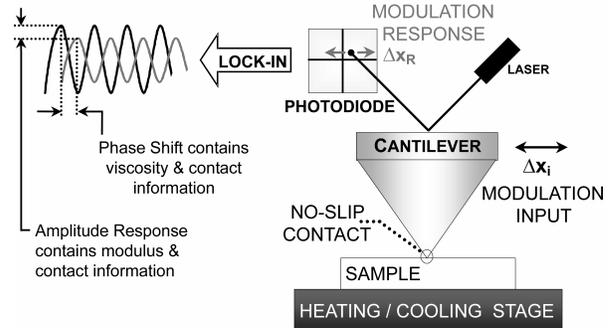


Figure 4: Working principle of shear modulated force microscopy

SM-FM is especially well-suited for surface thermo-rheological studies and has proven to be particularly successful in determining crosslinking densities and structural phase transitions in polymeric systems.^{24,25} Glass transition temperatures (T_g) are acquired by measuring contact stiffness changes with temperature, i.e. contact area changes occur only due to temperature induced changes in the sample modulus.²⁶ While the accuracy of SM-FM T_g measurements compares well with other techniques,²⁷ SM-FM offers the spatial resolution necessary to probe materials in confined sample geometries, allowing us to explore molecular constraints in nanoscopic systems.

3. MOLECULAR CONSTRAINTS

Macromolecules reside within a complex potential energy landscape, comprised of all the interactions they have with their own constituent atoms, along with those of their neighbors. The neighboring environment could be *self-similar*, in the case of a bulk material, or *a-similar*, when the system includes blends, interfaces, or localized ensembles of a particular nanoscale device. The *apparent* system properties, depend on how the molecules *move* within their energy landscapes. They move through various relaxation modes, which are pinned to the underlying degrees of freedom associated with their collective interactions. Constraints that restrict these freedoms, either internal (chemical, structural) or external (dimensional, interfacial), are manifested in the material properties.¹⁶

3.1 Internal constraints: chemical and structural

Internal constraints are inherent to molecular architecture, and generally result from direct bonding, dipole interactions, or steric effects. This type of constraint can be incorporated *a priori* into molecular designs, as a prescription for desired material properties. For example, by reducing the crosslink spacing in polymers, the naturally

occurring molecular relaxation may be confined in order to control the yield stress of organic thin-films. This is illustrated in Fig. 5 for the polymer media in a terabit-recording NEMS application, which exhibits a critical crosslinking spacing δ_c below which, the wear mechanism is dominated by the crosslink density.²⁸

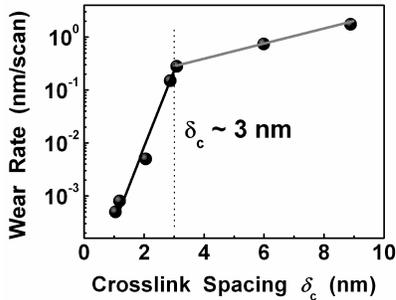


Fig. 5: A transition between wear modes in polystyrene occurs when the crosslinks spacing δ_c matches the length scale required for segmental backbone relaxation ξ_{α} . Below $\delta_c \sim 3$ nm, internal constraints interfere with native relaxation & wear is highly sensitive to the crosslink density. Above 3 nm, native relaxation can occur relatively unimpeded between dilute internal constraints; thus, there is little wear dependence on δ_c .²⁸

The transition between wear modes occurs when the spacing between crosslinks δ_c matches the length scale required for segmental backbone relaxation ξ_{α} . When the crosslink spacing falls below the cooperation length ($\delta_c < \xi_{\alpha}$), constraints are imposed on backbone mobility, essentially stiffening the material. Under these conditions, increased hardness and reduced wear are strongly correlated with crosslink spacing. If the concentration of crosslinks is insufficient to interfere with natural backbone relaxation ($\delta_c \gg \xi_{\alpha}$), the crosslinks have little impact on the polymer response and the material behaves similar to the uncrosslinked native.

3.2 External constraints: dimensional and interfacial

In addition to internal constraints, nanoscopic systems are subject to external constraints. External constraints stem from the interactions a molecular system has with its boundaries. They often arise in the vicinity of interfaces or other hetero-junctions, and propagate over a finite distance. As a result, external constraints can generate non-uniformities like material anisotropy or local entropic cooling (i.e. preferential structuring), both with direct impact on system properties. In polymer thin films, for example, interfacial glass transition temperature profiles mapped with SM-FM reveal a two-phase rheological boundary layer that extends over 100 nm beyond the substrate interface,²⁹ Fig. 6.

In spin-cast polymer thin-films, interfacial interactions lead to the formation of a less dense *sublayer* adjacent to the interface. The thickness of the sublayer is characterized, in part, by the molecular dimensions and the interaction potential at the interface. The coupled effects of shear-

induced structuring during spin casting and anisotropic relaxation during annealing create an *intermediate regime* between the sublayer and bulk phase. The overall boundary may extend two orders of magnitude beyond the polymer's persistence length; molecular restructuring within the boundary is thermally stable well above T_g .²⁹

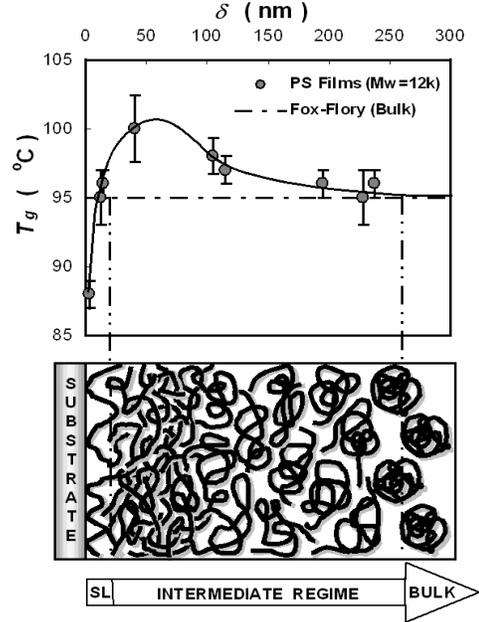


Fig. 6: (top) Film thickness, δ dependence of T_g for PS films ($M_w = 12k$) compared to the bulk T_g from Fox-Flory theory. (bottom) Rheological boundary model for the anisotropic structuring associated with the observed $T_g(\delta)$ profile (SL = sublayer).²⁹

When internal constraints are incorporated within the interfacial system, in the form of crosslinks, the T_g profiles are shifted away from the interface.²⁹ Thus, with judicious placements or omissions of internal constraints, it is possible to regulate a system's response to external constraints. In other words, nanoscopic systems experience an interplay between internal and external constraints. In order to discern a balance between the two, it is necessary to inquire locally how molecules behave, *in-situ*, within their potential landscape.

4. NANOSCALE APPLICATIONS

Having established a foundation and classification for nanoscopic constraints, we consider their impact on device performance, and return to the NEMS terabit data-storage^{1,2} application. Recalling from section 3.1, that polymer media wear can be reduced by confining molecular relaxation with the addition of internal constraints, we examine external constraints in the nanoscopic system of a recorded datum-bit. Bit writing involves a high-speed (kHz/probe) nanoindentation process into a substrate-supported, polymer thin-film, Fig. 7. With a similar set-up, using a single SPM probe, we investigated the strain within substrate supported polystyrene (PS) thin films.

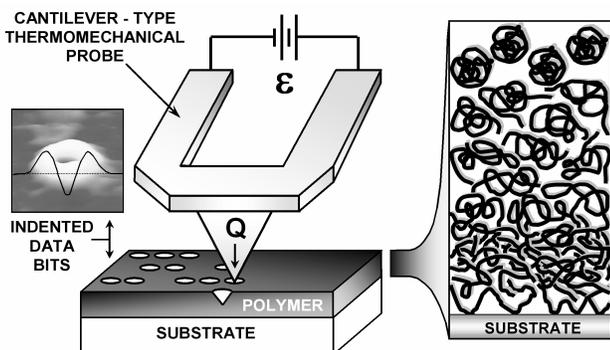


Fig. 7. Terabit storage with thermomechanical SPM probes: Controlling bit indentations in sub-100 nm thick polymer media must account for the interplay between internal and external constraints.

SPM nanoindentation studies reveal substantial strain shielding at the PS-substrate interface, which can lead to undesired rim formation during indentation.³⁰ Anisotropy generated by external constraints at the substrate leads to a distribution of indentation pressures between two asymptotic scenarios: (i) a compliant surface with a rigid sub-surface and (ii) a rigid surface with a compliant sub-surface.³⁰ In Fig. 8, the interfacial elastic-modulus profiles from the nanoimpact studies match the SM-FM T_g - profiles in Fig. 6. An increase in T_g implies a more rigid backbone, which is accompanied by an increased modulus; thus, thermal and mechanical responses should coincide.

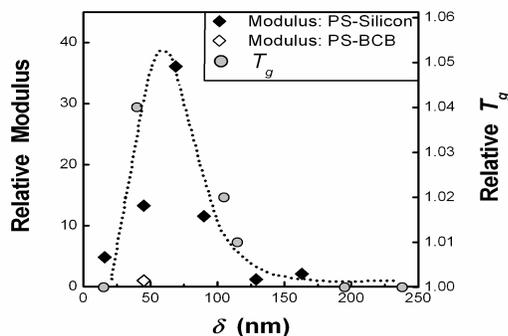


Fig. 8: Interfacial thermal and mechanical profiles for thin polystyrene films are consistent with the anisotropic boundary model in Fig. 6.³⁰

Regarding device performance, increased rim heights are observed for film thicknesses between 60-120 nm because elastic strain and plastic flow are constrained by the more rigid sub-surface. When the film thickness falls below ~ 60 nm, decreased rim heights are expected because the indentation load is accommodated by the strain or flow of a more compliant sub-surface. Thus, the film thickness can be optimized to minimize rim formation. Alternatively, internal constraints could be incorporated into the molecular design^{28,29} to shift the transition between the opposing structural gradients. In either scenario, we strive to reach a delicate balance between a molecular system and its interactions with its boundaries.

5. OUTLOOK

Critical to nanoscale material design is the ability to tailor system properties by controlling the internal degrees of freedom available for molecular relaxation. On one hand, external constraints imposed at interfaces and system boundaries generate structural and dynamical anisotropy that propagates over relevant length scales. On the other hand, the ability to cater relaxation behavior through molecularly-engineered internal constraints offers a path to optimize material properties in nanoscopic systems.

Efforts to develop a balance between external and internal constraints benefit from the real-space sensitivity afforded by quantitative SPM techniques. FFM and SM-FM investigations of polymer dynamics near interfaces provide activation energies related to molecular relaxation, and offer insight into the effects of constraints on structural relaxation and the resulting material properties.

REFERENCES

- G.K. Binnig, G. Cherubini, M. Despont, et al., in *Springer Handbook of Nanotechnology*, ed. B. Bhushan (Springer-Verlag, Heidelberg, 2004).
- P. Vettiger, G. Cross, M. Despont, et al., *IEEE Trans Nanotechnol* **1** (2002) 39.
- U. Tracht, M. Wilhelm, A. Heuer, et al., *Phys Rev Lett* **81** (1998) 2727.
- Y. Liu, T.P. Russell, M.G. Samant, et al., *Macromole* **30** (1997) 7768.
- B. Frank, A.P. Gast, T.P. Russel, et al., *Macromole*. **29** (1996) 6531.
- J.C. Jean, R. Zhang, H. Cao, et al., *Phys Rev B* **56** (1997) R8459.
- G.B. DeMaggio, W.E. Frieze, D.W. Gidley, et al., *Phys Rev Lett* **78** (1997) 1524.
- J.L. Keddie, R.L. Jones & R.A. Cory, *Europhys Lett* **27** (1994) 59.
- J.A. Forrest, K. Dalnoki-Veress & J.R. Dutcher, *Phys Rev E* **58** (1998) 6109.
- E.W. Fischer, A. Bakai, A. Patkowski, et al., *J Non-Crystalline Solids* **307-310** (2002) 584.
- J.A. Forrest, C. Svanberg, K. Revesz, et al., *Phys Rev E* **58** (1998) R1226.
- M.D. Ediger, *Annu Rev Phys Chem* **51** (2000) 99-128.
- C.M. Roland & R. Casalini, *J Chem Phys* **119** (2003) 1838-42
- H. Richardson, M. Sferrazza & J.L. Keddie, *Euro. Phys. J. E* **12** (2003) S87.
- O. Prucker, S. Christian, H. Bock, et al., *Macromolecular Chemistry and Physics* **199** (1998) 1435.
- S. Sills & R.M. Overney, in *Applied Scanning Probe Methods II*, eds B. Bushan & H. Fuchs (Springer-Verlag, Heidelberg, 2006).
- The experimental details of FFM can be found in reference 16.
- K.A. Grosch, *Proc R Soc London Ser A* **274** (1963) 21.
- K.C. Ludema & D. Tabor, *Wear* **9** (1966) 329.
- S. Sills, R.M. Overney, K. Vorvolakos, et al., in *Nanotribology: Friction and wear on the atomic scale*, eds E. Gnecco & E. Meyer (Springer-Verlag, Heidelberg, Germany, 2007), 659.
- J.A. Hammerschmidt, W.L. Gladfelter & G. Haugstad, *Macromole* **32** (1999) 3360.
- S. Sills & R.M. Overney, *Phys Rev Lett* **91** (2003) 095501(1-4).
- S. Sills, T. Gray & R.M. Overney, *J Chem Phys* **123** (2005) 134902.
- R. Luginbuhl, R.M. Overney & B.D. Ratner, *ACS Symposium: Interfacial Properties on the Submicrometer Scale* **781** (2001) 178.
- R.M. Overney, C. Buenviaje, R. Luginbuhl, et al., *J Therm Anal Cal* **59** (2000) 205.
- Experimental details of SM-FM can be found in reference 16.
- C. Buenviaje, F. Dinelli & R.M. Overney, in *Interfacial Properties on the Submicron Scale; Vol. 781*, eds J. Frommer & R.M. Overney (American Chemical Society, Washington, DC, 2000), 76.
- B. Gotsmann, U.T. Duerig, S. Sills, et al., *Nano Lett* **6** (2006) 296.
- S. Sills, R.M. Overney, W. Chau, et al., *J Chem Phys* **120** (2004) 5334.
- S. Sills, R.M. Overney, B. Gotsmann, et al., *Tribo Lett* **19** (2005) 9.