Introduction

• Mesoscale Research and Perception
• Novel Surface Technique: Scanning Force Microscopy
  (also called: Atomic Force Microscopy)
• Motivation for Mesoscale Research:
  - Confinement Effects in Thin Spincast Films
• Examples of Sensible Mesoscale Technologies:
  - Thin Film Lubrication \( \rightarrow \) Mesoscale Kinetics
  - Ultrathin LED Materials \( \rightarrow \) Exciton Annihilation
  - PEM Fuel Cell \( \rightarrow \) Proton Transport
Mesoscale Science and Technology

Applications:
- Lubrication
- Photonics
- Fuel Cells
- Data Storage

The realm of the Mesoscale fosters new perceptions and approaches.

Illustration of a 2D Phenomenon

A highly organized plastic deformation: often referred to as Schallamach Waves

AFM Scan:
Probe Width: ~ 10 nm
Line Separation: > 100 nm

- a slow moving (~ μm/s) sliding contact (~10^{-5} μm^2) affects a scan area on the order of 10^3 μm^2 in an apparently coherent fashion.
**Flatland**
An entertaining satire by Edwin A. Abbott

**A Sphere,**
an inhabitant from *Spaceland,*
introduces
**a Square,**
an inhabitant from *Flatland* to a higher Dimensionality


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**Flatland – An entertaining satire by Edwin A. Abbott**

**Perception**

*Dimensionality nurtures perceptions and limits possibilities.*

- Objects are perceived in Flatland as lines or points.

  ![Diagram of objects in Flatland](image)

- To distinguish objects in Flatland the observer has to travel around the objects.

  ![Diagram showing travel around objects](image)

* A Circle is perceived as an angularly length-invariant object.
* A Sphere is reduced to its cross-sectional area with Flatland, and thus, perceived as a Circle.
Boundaries in lower dimensionalities are lifted from the perspective of a higher dimensionality.

*Flatland: “Physical Laws”*

Abbott spent a significant part of his satire on developing the two-dimensional world of Flatland by introducing imaginary laws of nature that apply in one and 2-dimensions. Although these laws that for instance explain how rain is experienced in 2-dimensions are unrealistic, they impressively illustrate the mystery of lower dimensionalities.
Illustration of Dimensionality: Acoustic Wave (3D vs. 2D)

**Huygens Body Waves (3D solution)**
A spatially localized initial disturbance gives rise to a limited and fast decaying disturbance only, at any accessible location away from the source of the disturbance.

**Rayleigh Surface Waves**
Waves, propagating over the surface of a body with a small penetration distance into the interior of the body, acquire at a great distance from the source a continually increasing preponderance.

--> important in the study of seismic phenomena

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**NanoScience Tool**

**Atomic Force Microscopy (AFM)**

![AFM Diagram]

Material Distinction

Elasticity

Topography

Photodiode

Laser

Piezo

Cantilever

Sample

Glass Transition

$T_g = 374K$
**SFM Setup**

In environmental chamber with sample heating /cooling stage

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Confined Boundary Layer of Spincast Films

*Latera Force and Dewetting Studies* suggest that the PEP phase is rheological modified within a 100 nm boundary region that exceeds by two orders of magnitude the theoretically predicted pinning regime of annealed elastomers at interfaces with negative spreading coefficient.

<table>
<thead>
<tr>
<th>Classical</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean field theories consider the effect of pinning at interfaces only within a pinning regime (0.6 - 1 \text{ nm} \ll R_g)</td>
<td>~ 100 nm</td>
</tr>
<tr>
<td>~ 1 nm</td>
<td>Diffusion into</td>
</tr>
<tr>
<td></td>
<td>Disentangled Sublayer</td>
</tr>
</tbody>
</table>
Glass Transition Properties of Confined Films

Glass transition studies on polystyrene indicate confinement effects similar to those found in PEP shear studies.

Near-Surface \( T_g \) Measurements of "Thick" Films (t > 100 nm) are bulk-like.


![Diagram of glass transition properties and confinement effects](image)

Lubrication

**Liquid Structuring: Entropic Cooling**

- Interfacial confinement leads to an entropically cooled boundary layer in simple fluids like hexadecane.

- Shear Modulated SFM approach curves indicate a hexadecane boundary layer thickness of ~2.5 nm on \( \text{SiO}_2 \).

- Molecular Dynamics simulations predict a boundary layer thickness of 1.5-1.8 nm.

![Diagram of liquid structuring and entropic cooling](image)
Examples of Sensible Mesoscale Technologies

- **Thin Film Lubrication**
  → *Mesoscale Kinetics*

- **Thin Film LED Materials**
  → *Exciton Annihilation*

- **PEM Fuel Cell**
  → *Proton Transport*

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**Mesoscale Kinetics - Fractal Bonding Kinetics and Lubrication**

*Monolayer Lubricant:* Hydroxyl-terminated perfluoropolyether (PFPE-OH) film (Fomblin Zdol©)

*Interaction:* Hydroxylated chain ends form hydrogen bonds with carbon surface.

*Lubrication Performance:* Depends on the molecular mobility

\[
X - (\text{CF}_2\text{O})_y (\text{CF}_2\text{CF}_2\text{O})_z \text{CF}_2 - X
\]

- X: CH$_2$OH (functional group)
- y: perfluoromethylene oxide groups (C1)
- z: perfluoroethylene oxide groups (C2)
Monolayer Lubrication and Kinetics

i. The monolayer confined system exhibits a glass transition value of 52 °C that is significantly exceeding the bulk material value of -115 °C.

ii. The confined system exhibits a “Fractal Reaction Kinetics”.

iii. The rheological transition at 52 °C separates two fundamental kinetic bounding regimes:
   - diffusion limited reaction
   - activation barrier limited reaction

iv. The shear rheological analysis with SM-SFM was found to provide valuable material information that explains the “exotic” reaction kinetics.
Photonics and Thin Semiconducting Polymer Films

Motivations for Mesoscopic Rheological Analysis:

- Film preparation parameters have shown to effect significantly the optoelectronic properties (e.g., conversion temperature)
- Ultrathin films have shown very exotic optoelectronic properties (bias-voltage dependent color emission)

Bias-voltage dependent Reversible Color Emission

Thickness dependent Luminescence

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>Thickness</th>
<th>Bias Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyquinolines</td>
<td>n-type</td>
<td>67 nm</td>
<td>10-30 V: orange-red</td>
</tr>
<tr>
<td>Polyphenylenes</td>
<td>p-type</td>
<td>25 nm</td>
<td>8-10 V: orange, 13-20 V: green</td>
</tr>
</tbody>
</table>

**Film Preparation of PPV**

PPV is not soluble in conventional solvents used for spin coating. A two-step process is needed, which involves a tetrahydrothiofenium (THT) precursor polymer, which is soluble (e.g., in methanol). After spin casting the film is converted by thermal annealing into PPV.

- Silicon substrates: cleaned sequentially with acetone and methanol
- THT films: spin coated at 1000 rpm onto Si (sulfonium precursor in a methanol solution, 1 wt%)
- Conversion in vacuum oven at 10°C/min starting from 100°C.
- Samples were cooled to room temperature at a rate of approximately 40°C/min

**Rheological Transition Measurements**

- Conversion Temperature: 175 °C
- $T_g = 66$ °C
- Conversion Temperature: 175 °C

\[ \text{SHEAR RESPONSE} \quad \leftrightarrow \quad \Delta \chi_R \]

\[ \text{HEATING / COOLING STAGE} \]

\[ \text{SAMPLE} \]

\[ \text{CANTILEVER} \]

\[ \text{NO-SLIP CONTACT} \]

\[ \text{SHEAR DISPLACEMENT, } \Delta \chi_{\text{MOD}} \]
Qualitative comparison of
(a) the rheological transition temperature $T_g$ (measured with the SM-SFM method) with
(b) the photo-luminescence (PL) efficiency


as function of the PPV conversion temperature.

**Photoluminescence Efficiency vs. Glass Transition**

<table>
<thead>
<tr>
<th>Transition Temperature (°C)</th>
<th>PL Quantum Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>0.085</td>
</tr>
<tr>
<td>60</td>
<td>0.105</td>
</tr>
<tr>
<td>65</td>
<td>0.125</td>
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<tr>
<td>70</td>
<td>0.145</td>
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<tr>
<td>75</td>
<td>0.165</td>
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<tr>
<td>80</td>
<td>0.185</td>
</tr>
<tr>
<td>85</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>


**Interpretation**

Below 205 °C, the degree of conversion to PPV (which is increasing with temperature) is dominating both, the rheological transition properties and the EL efficiency.

Above 205 °C, polymer degradation is dominating. For instance, it is known that carbonyl groups are formed excessively (Morgado, J., F. Cacialli, et al. (1999). J. Appl. Phys. 85 (3): 1784-1791).

**Effects on Rheological Transition:**
- (left) Degree of conversion to PPV increases thermal transition values
- (right) Degradation lowers the transition values

**Effects on EL Intensity:**
- (left) Degree of conversion to PPV increase EL intensity.
- (right) Residual byproducts from conversion and oxygen degradation act as exciton quenching sites (radiation-free annihilation), i.e., lower the EL intensity.
Proton Exchange Membrane (PEM) Fuel Cell

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PEM Fuel Cell

\[ 2H^+ + 2e^- + O_2 \rightarrow 2H_2O \]

\[ 4H^+ + 4e^- + O_2 \rightarrow 2H_2 \]

Nafion: Commercially available perfluorosulphonate cation exchange membrane

\[ -\left(\text{CF}_2-\text{CF}_2\right)_x \left(\text{CF}_2-\text{CF}_2\right)_y \left(\text{O-CF}_2-\text{CF}_2\right)_m \text{O-CF}_2-\text{CF}_2-\text{SO}_3\text{H} \]

Nafion consists of a hydrophobic tetrafluoroethylene (TFE) backbone with pendant side chains of perfluorinated vinylethers terminated by ion-exchange groups. → Ionic Cluster Model involving sulphonate groups.

Polymer relaxation properties affect the proton transport properties.