Structure and Dynamics of Polymer Nanocomposites by Grazing-Incidence X-Ray Techniques

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Advanced Photon Source

- 3rd generation synchrotron x-ray facility built by US DoE for basic and applied research
- 3000 Users/Year: physics, chemistry, materials science, biology, energy …
Outlines

- Scientific opportunities and motivations
- Structure, kinetics and self-assembly in thin films of polymer nanocomposites
  - Anisotropic nanoparticle diffusion and dynamics in ultrathin polymer films
  - Self Assembly of 2D diblock copolymer single crystal by graphoepitaxy
  - Diblock copolymer/nanoparticle self assembly
- Ionic distribution near membrane surfaces using x-ray standing waves
- Membrane research with surface sensitive x-ray techniques
**Motivations**

- Self-assembly of nanostructure is mostly an art.
- The self-assembly is NOT an equilibrating process.
- A controlled self-assembling needs to be guided by a thorough understanding of ordering kinetics.

**Nanoparticle Diffusion in Ultrathin Polymer Films**

- Understanding the diffusion of nanoparticle metal particle in ultrathin polymer films
  - molecular dynamic in confined geometry
  - drastically different diffusion properties than in bulk
  - van der Waals interactions, steric forces, chemical affinities

- A host of x-ray techniques can be applied
  - Reflectivity and standing waves: diffusion perpendicular to interfaces
  - X-ray photon correlation spectroscopy: local short time dynamics
  - GISAXS using x-ray wave-guides: in-plane motion

- Complementary techniques
  - TEM
  - SPM
Grazing-Incident Techniques - X-ray Reflectivity and More

- Nanoparticles embedded in polymer films

**GISAXS with Enhancement**

- Scattering in x, y, z directions reveals the sample structure in 3D
- Enhancement due to waveguides is apparent at different incident angles

Real-Time Measurements: Kinetics

- Particle lateral diffusion reveal by $q_{//}$ scans

- Nanoparticles are moving faster in plane
- This constitutes the base of forming self-assembly in 2D
Dynamics of Nanoparticles in Polymer Films

- Dynamics of single nanoparticles ultimately determines their diffusion
- Dynamical light scattering (DLS) is not effective because of q-range
- X-ray photon correlation spectroscopy (XPCS) is well-suited
- X-ray beams at the APS can be effectively used for XPCS (8-ID).

\[
g_z(\bar{Q}, t) = 1 + A \frac{\langle I(\bar{Q}, t) I(\bar{Q}, t + \tau) \rangle_r}{\langle I(\bar{Q}, \tau) \rangle_r^2}
\]
**XPCS Results**

- Au nanoparticles on MW 120K 700 Å PS

- Exhibits Ballistic motion with a Drift Velocity $1/(\tau Q)$ of $\sim 0.1$ Å/sec

- Such behavior observed in systems aging with time viz. colloidal glass, gels ...

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Self Assembly of Diblock Copolymer 2D Crystals

- Samples: PS-P2VP thin film
- Substrate: patterned surface
- Graphoeptaxy

Stein et al, PRL 98 086101 (2007)
Diblock Copolymer/Nanoparticle Co-Self-Assembly

- Nanoparticle-facilitated PS-P2VP self assembly (CdSe particle)
  - Nanoparticle changed the energy state and phase diagram of the system

Before Anneal

X-ray Standing Waves

X-Ray Standing Waves by Total External Reflection

Standing Wave Period:

\[ D = \frac{\lambda}{2 \sin \theta} \]
**Charged Membrane Surfaces**

- Charged membrane in contact with electrolytes (ion transport)
- Model by Helmholtz, Gouy-Chapman, Stern

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**Diagram:**

- Membrane surface with net negative charge
- Electrolyte
- (+) Counterion
- (-) Coion
- Concentration vs. depth
- Polypropylene (6 μm)
- ZnCl₂ Solution (2 μm)
- Phospholipid (27 Å)
- Silane (4 Å)
- Si (25 Å)
- W (9 Å)

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**Text:**

Bedzyk, Bommarito, Caffrey, Penner, Science 248, 52 (1990)
DDL Reversibility by pH

- As H+ concentration increased, the amount of zinc in the DDL decreased
- Recovery of the pH 5.8 distribution profile was essentially complete

Jin Wang, Martin Caffrey, Mike Bezyk, Tom Penner
Langmuir, 17. 3681 (2001)
Ionic Distribution Near Polymer Brush/Membrane

Standing wave measurements can yield the Br ion distribution between membranes.

Rafael Bras, Yan Sun of Ken Shull’s group @ Northwestern U.

← in aqueous Potassium Bromide solution environment (KBr); Langmuir-Blodgett (LB) method for obtaining PS-PEO layer

Preliminary results:
Summary

- Surface Sensitive X-ray Techniques suitable for membrane structure/kinetics/dynamics characterization
  - Reflectivity (XRR)
  - Diffuse scattering
  - X-ray standing waves (XSWs)
  - Grazing-incident small angle scattering (GISAXS)

- Nonintrusive, in situ capabilities
- Sensitive for thin films

Practical Challenges

Fundamental and understanding is necessary to control the formation of membranes on all length scales and time scales

Organic-membranes: Polymeric matrix and composites
Nature of Hydrophilic/hydrophobic interaction for fouling
Specific and nonspecific adsorption and absorption
Porosity control
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