X-Ray Studies of Diffusion Dynamics in Nano-Confined Geometries

http://xkcd.com/1403/

IN CONCLUSION, AAAAAAAAAAAA!!!

THE BEST THESIS DEFENSE IS A GOOD THESIS OFFENSE.
Outline

• Introduction
• Techniques
  – Langmuir-Blodgett Films
  – X-Ray Photon Correlation Spectroscopy (XPCS)
• Results
  – Non-Equilibrium Dynamics
  – Aging
  – Jamming Transition
• Conclusion
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You do not really understand something unless you can explain it to your grandmother.

Leandra, a lot of things are nanotechnology. Tennis balls are nanotechnology. Even *humans* are nanotechnology!

If you really understand something, you can afford to explain it using language that can be easily understood.

Ongoing process
Ways to Look at Small Things

Optical Microscopy
>100nm

Diffraction Limit
\[ d \sim \lambda \]

De Broglie Wavelength
\[ \lambda = \frac{h}{p} \]

Scanning Electron Microscopy
>1nm

Transmission Electron Microscopy
>1Å
Why X-Rays?

- Wavelength (10pm-10nm)
- Penetrating
- Non-Invasive
- Global, Statistical Information
- \textit{In situ} Studies
- Surface Sensitivity (GID)
- Coherence (XPCS)
10nm iron oxide nanoparticle film during compression on liquid surface

How do individual particle dynamics affect the film structure?
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Liquid Surface Self Assembly

- Van der Waals Force
- Interfacial Forces
- Magnetic Interactions
- Electric Interactions

Langmuir-Blodgett Trough

chloroform

pressure sensor

Teflon trough

barrier

pure water
Monolayers
Macroscale Self-Assembly (Cheerios Effect)
Macroscale Compression
Isotherms
The Microscopic Picture

20nm particles, $\Pi \sim 5\text{mN/m}$

20nm particles, $\Pi \sim 15\text{mN/m}$

20nm particles, $\Pi \sim 40\text{mN/m}$

5nm particles, $\Pi \sim 40\text{mN/m}$
The Nanoscopic Picture

???
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Grazing Incidence Diffraction (GID)

\[ n\lambda = 2d \sin \theta \]
Coherent Speckle

Experimental Location
SYNCHROTRONS.

They generate pure and more complete patterns than X-ray beams. Data collection takes a fraction of the time.
X-Ray Photon Correlation Spectroscopy (XPCS)
Timescales

How *old* is the film? (age) - hours

How *quickly* are the particles moving? (dynamics timescale) – hundreds of seconds ($\tau$)
Experimental Setup

im in ur beamlinez

stealin ur x-rayz
Interparticle Dynamics

\[ g_2(\Delta t) = \frac{\langle I(t)I(t + \Delta t) \rangle_t}{\langle I(t) \rangle_t^2} \]

No motion – constant intensity
Motion – changing intensity, decorrelation

\[ g_2(\Delta t) - 1 = b \left[ Ae^{-\left(\frac{t}{\tau}\right)\beta} \right]^2 \]

\[ \beta = 1 \text{ (here)} \]
\[ \tau = \text{“characteristic timescale” or “relaxation time”} \]
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Nanoscale Grain Boundaries

(a) 60µm

(b) 0.6µm

Macroscale Grain Boundaries
Experimental Procedure

- Compress to specific surface area
- STOP compression (hold barrier in place)
- Measure diffusion of particles using XPCS for several hours
- Make new film
- Repeat for different surface area
Pressure Post-Compression

\[ II = ae^{-t/\tau_1} + be^{-t/\tau_2} + ce^{-t/\tau_3}. \]

<table>
<thead>
<tr>
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<th>Film 3</th>
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<tr>
<td>(\tau_1) (s)</td>
<td>90</td>
<td>60</td>
<td>160</td>
</tr>
<tr>
<td>(\tau_2) (s)</td>
<td>1.2e3</td>
<td>1.7e3</td>
<td>2.1e3</td>
</tr>
<tr>
<td>(\tau_3) (s)</td>
<td>-1.3e5</td>
<td>3.5e5</td>
<td>2.4e5</td>
</tr>
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Things are moving. So what?

- Interparticle spacing changed by < 2Å (1%)
- Level of disorder varied by < 15%
Diffusion Timescales

\[ g_2(\Delta t) - 1 = b \left[ A e^{-\left(\frac{t}{\tau}\right)^\beta} \right]^2 \]

Aging Time (s)

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Effect of Stretching Exponent

- **glass**
- **Brownian diffusion**
- **jammed system**
- **same $\tau$ value**

The graph shows the effect of different stretching exponents ($\beta$) on the behavior of a system, with $\beta=1$ (Regular), $\beta=0.5$ (Stretched), and $\beta=1.5$ (Compressed).
Jamming (colloquially)
Jamming (physics)

Jamming - an arrangement of particles undergoes structural arrest, transforming from a colloidal suspension into a disordered solid characterized by a yield stress, as the phase space no longer supports macroscopic motion.

Glass transition – occurs with temperature
Jamming transition – occurs with density (pressure)

Examples:
• Sand
• Macaroni or rice
• Traffic jams
Effect of Stretching Exponent

glass

Brownian diffusion

jammed system

same $\tau$ value

$\beta=1$ (Regular)

$\beta=0.5$ (Stretched)

$\beta=1.5$ (Compressed)
Avalanches in Jammed Systems

https://www.youtube.com/watch?v=5cgQoUMd-s4
2-Time Autocorrelation

\[ g_2(\Delta t) = \frac{\langle I(t)I(t + \Delta t)\rangle_t}{\langle I(t)\rangle_t^2} \]

\[ g_{2,2-time}(\Delta t_1, \Delta t_2) = \frac{\langle I(t + \Delta t_1)I(t + \Delta t_2)\rangle_t}{\langle I(t)\rangle_t^2} \]
Avalanching

0.23-0.42 hrs

0.61-0.80 hrs

1.3-1.45 hrs

3.9-4.1 hrs

Film age

$g_{2,2t}$
Pressure-Dependent Trends

![Graph showing pressure-dependent trends with film 1 (20 mN/m), film 2 (30 mN/m), and film 3 (40 mN/m). The graph plots aging time (s) against the coefficient β.]
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Conclusion

• Jammed system
• Non-equilibrium dynamics
• Clear signs of aging

During aging:
• No change in interparticle spacing
• No change in disorder
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- Suresh Narayanan (APS/S8)
- Alec Sandy (APS/S8)
“Call me when the bomb squad gets here, I want to take pictures for Oleg’s tenure file.” –Dmitri Basov, November 2012
Thank You!
Backup Slides
Graphs
40mN Film
Autocorrelation Curves

$g_2$ vs $\Delta t$ (s)

- 0.23 hrs
- 0.42 hrs
- 0.61 hrs
- 0.8 hrs
- 2.3 hrs
- 5.1 hrs
Radiation Damage

X-Ray Beam

“hard” core

“soft” coating

Specular Reflectivity

Intensity vs. Time (s)

GID Peak After Successive 500s Exposures

Intensity vs. dθ
In-Plane Film Structure

Nearest Neighbor Spacing

<table>
<thead>
<tr>
<th></th>
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<th>2nd</th>
<th>3rd</th>
<th>4th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal Close Packed</td>
<td>1</td>
<td>$\sqrt{3}$</td>
<td>≈1.73</td>
<td>2</td>
</tr>
<tr>
<td>Experiment</td>
<td>1</td>
<td>1.75</td>
<td>2.01</td>
<td>2.74</td>
</tr>
</tbody>
</table>
Why Iron Oxide?

"This dye was selected because the bottle was within reach"
#overlyhonestmethods