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What shall I talk about

- **R** Probing Materials with Radiation
- ℜ Systems that can be probed
 - **G** Crystalline
 - Amorphous including glasses
 - Soft materials including liquids and bio-materials
 - 3 Nanomaterials
 - **Superlattices and multilayers**
 - *Materials at interfaces*
- Radiation for probing
 - Sub-optical (mid and far Infrared)
 - 😋 Optical (near Ultraviolet, Visible, near Infrared)
 - Ultraviolet (vacuum to extreme)
 - Soft and Hard X-rays
 - 🕝 Gamma rays

Matter-Radiation Interactions

CR Elastic
 CS Diffraction
 CS Reflection
 CS Diffuse Scattering
 CInelastic
 CS Absorptive
 CS Raman Scattering
 COmpton Scattering

Elastic Scattering Techniques

- Depend on the interference of scattered waves, *electromagnetic or matter*, which creates variation in scattered intensity depending on incident and scattering angles.
- Reference of the wavelength, $n_i(n_s)$ is the refractive index in medium of incidence (scattering) and $\alpha_i(\alpha_s)$ is incident (scattered) angle, then we define incident and scattered wave vectors as $k_i = (2\pi/n_i\lambda)\text{Sin}\alpha_i$ and $k_s = (2\pi/n_s\lambda)\text{Sin}\alpha_s$ and the scattered intensity *I*, is dependent on the momentum transfer $q = k_s k_i$
- Reference in all scattering studies, we analyze I(q) to get information of structures that give rise to this functional form.

Reciprocal Space

○ If r_1 and r_2 are two points on a lattice, the lattice vector

$$R=r_2-r_1$$

 \bowtie We can always construct a set of equi-spaced parallel planes containing all the lattice points and having a normal G. Phase correlation between G and R

 $e^{G.R} = 1$ or $G.R = 2\pi m, m = 0, \pm 1, \pm 2, ...$

- α If $G = hb_1 + kb_2 + lb_3$, where *h*, *k*, *l* are integers, the above condition gives $a_i \cdot b_j = \delta_{ij}$
- \bowtie and the triad (b_1 , b_2 , b_3) is given by
- $\bowtie b_1 = \frac{2\pi(a_2 \times a_3)}{[a_1.(a_2 \times a_3)]'}$ and cyclic permutations

Convolutions

- □ CR Let us take a one-dimensional case
- A particle at *a* means probability

$$p(x) = \delta(x-a)$$

Real Bravais lattice with lattice constant *a* means probability

$$f(x) = \delta(x - na), \qquad n = 0, \pm 1, \pm 2$$

- Real of the particle is replaced by an object with 'shape' $\varphi(x)$, the probability is convoluted by this shape
- \bigcirc For object centered at a_i ,

$$p(x) = \int \varphi(x') \delta((x - x') - a) dx'$$

For a Bravais lattice with lattice constant *a*

$$p(x) = \int \varphi(x') \delta((x - x') - na) dx', \qquad n = 0, \pm 1, \pm 2, ...$$

In three-dimensions

$$p(\mathbf{r}) = \int \varphi(\mathbf{r}') \delta((\mathbf{r} - \mathbf{r}') - \mathbf{s}) d\mathbf{r}'$$

Convolution of functions f and g is defined as $f \otimes g = f(x)g(x-x)dx'$

Probability ~ density as measured by diffraction techniques.

How to get the shape (or structure) of the object and the Bravais lattice separated? This is 12/4/20known as deconvolution. We need to go to the reciprocal space. 6

Correlations

C Two particles at r₁ and r₂ are correlated if C(r₁,r₂) = <p(r₁)p(r₂)> = (1/V)/p(r₁)p(r₂)dr₁dr₂ ≠ 0
C For a perfect crystal C(0,r) = K, a constant
C For real crystals, C(0,r) = K exp(-r/ξ), i.e. the crystal is perfect when r<<ξ, ξ is the correlation length
C For two-dimensional crystals, C(0,r) ~ r(-h/ξ), h being a positive fraction; there is an inherent algebraic decay in correlation with distance
C For fluids, C(0,r) = C(0,r) ~ ρ₁², the average number density as r becomes large

Real How do correlations change in the reciprocal space?

Fourier Transform

 \bigcirc Fourier transform of the function f(x) and inverse Fourier transform. $\mathfrak{S}(f(x)) = f'(x) = (1/2\pi) \int exp(-ikx)f(x)dx;$ $\mathscr{V}(f(x)) = \int exp(ikx)f'(x)dx$ **C** In three dimensions, $\mathcal{F}(f(r)) = f'(r)$ $= (1/2\pi)^{3} \int exp(-i\mathbf{k} \cdot \mathbf{r}) f(\mathbf{r}) d\mathbf{r};$ $\Re \ (f(\mathbf{r})) = \int exp(i\mathbf{k}.\mathbf{r})f'(\mathbf{r})d\mathbf{r}; \mathbf{k}$ is the wavevector. Reverse Hence Fourier transform and its inverse connect real and reciprocal space

Properties of Fourier Transform

- $\textcircled{\ } \textbf{Call Constrainty: } \mathcal{I}\left(af(x) + bg(x)\right) = a \, \mathcal{I}(f(x)) + b \, \mathcal{I}(g(x))$
- $\mathfrak{Shift:} \ \mathfrak{I}(f(x+a)) = exp(-ika) \mathfrak{I}(f(x))$
- Convolution Theorem: $\Im(f \otimes g) = 2\pi \Im(f) \Im(g)$. This gives an easy way to deconvolute data
- Reference From shift property we get, for a particle, $\Im(\delta(x-a)) = (1/2\pi)exp(-ika)$, a delta function (particle) in reciprocal space
- For a one-dimensional Bravais lattice, ℑ(δ(x-na)) = $(1/2π) \sum exp(-inka)$, a lattice of particles in reciprocal space, which corresponds to the reciprocal lattice

Elastic Scattering

- A system of identical particles with positions *r*, incident (scattered) wavevector $k_i(k_s)$ of magnitude $k = 2\pi/\lambda$, position of detector from particle (centre of mass) = $R(R_0)$
- ↔ Scattering from point *r*: $dE = E_e exp(ikR)/R$
- \bowtie The emitted wave $E_e = c\rho_n(\mathbf{r})E_i = c\rho_n(\mathbf{r})E_0exp(i\mathbf{k}_i\cdot\mathbf{r})$
- $\text{ If } r << R_0, R \approx R_0 k_s r/k, dE = c \rho_n(r) E_0 exp(i(k_i k_s) r + ikR_0)/R_0$
- Summing over the atoms $E = c \left[exp(ikR_0)/R_0 \right] E_0 \int \rho_n(\mathbf{r}) E_0 exp(-iq.\mathbf{r}) d\mathbf{r}$, which is the Fourier transform of number density
- \curvearrowright The scattered intensity $I(q) \sim \int \rho_n(r') \rho_n(r'') exp(iq.(r'-r'')) dr' dr''$
- Representation Putting r = r'' r' and recognizing that $\int \rho_n(r') dr' = V < \rho_n(0) >$, we get $I(q) \sim < \int \rho_n(0) \rho_n(r) \exp(iq.r) dr >$

 $= \int \rho_n(0) \ \rho_n(\mathbf{r}) \ \exp(i\mathbf{q}.\mathbf{r}) \ d\mathbf{r} = \Im \left(C_d(\mathbf{r}) \right),$

Fourier transform of density-density correlation $C_d(\mathbf{r}) = \langle \rho_n(0) \rho_n(\mathbf{r}) \rangle$

Grazing Incidence Diffraction



In GID technique, a total external reflection occurs at the interface,

 $\alpha < \alpha_c$

 α = incidence angle

 α_c = the critical angle (~ milliradians for X-rays)

Field decays to 1/e of its value at top within a depth of $l \approx \lambda / [2\pi (\alpha - \alpha_c)^{1/2}]$

At these incident angles (~ milliradians) *I* is independent of λ and \approx 25 Å to 100 Å, inversely as electron density of medium

Condition for GID:

Incident X-rays are confined to ~ 100 Å below interfacial plane, whereas they travel in the plane (x and y directions) with a wavelength close to the free-space wavelength

Our Materials: Amphiphiles



Some Amphiphiles

1. The Whalelephant



Our Systems: Langmuir Monolayers



If an amphiphile is dissolved in some liquid which has Surface Tension, Density and Boiling Point much less than Water and a Very Small Amount of this Dilute Solution is Spread on Water

Then after the Solvent Spreads Evenly over the Water Surface and Evaporates

The Amphiphiles form a Monomolecular Layer at the Air Water Interface with Heads in Water and Tails in Air

This is the LANGMUIR MONOLAYER - Perhaps the Most Easily Achievable Two-Dimensional System

Monolayer Phases

A Langmuir Monolayer can be compressed two-dimensionally by pushing a mechanical barrier across the water surface

The compressed monolayer becomes denser and its surface tension (measured generally by Wilhelmy Plate) gradually reduces from that of pure water to that of pure hydrocarbons (oils)

This drop in surface tension is called SURFACE PRESSURE and is the measured two-dimensional analogue of pressure

 $\pi = \gamma_{water} - \gamma_{monolayer}$

When surface pressure is plotted as a function of the area per amphiphile molecule in the monolayer (A), we get a π -A isotherm which is again the two-dimensional analogue of the p-V Isotherm of a three-dimensional system

The π -A isotherm shows discontinuities such as abrupt changes in slope (kinks) and straight sections which were thought to be and are now known to be Phase Transitions

GID Studies of Langmuir Monolayers

The Different Monolayer Phases have different 2D Lattices

These can be studied by GID



Schematic View of Set-up



Actual Set-up at NSLS and APS

The Basic Equations

The Langmuir Monolayer has randomly oriented domains in the horizontal plane hence x and y directions are not resolved

 $K_{xy} = (k_{xy}^{f^{2}} + k_{xy}^{i^{2}} - 2 k_{xy}^{f} k_{xy}^{i} \cos 2\theta)^{\frac{1}{2}}$

 $= 2\pi/\lambda \left(\cos^2\alpha_i + \cos^2\alpha_f - 2\cos\alpha_i\cos\alpha_f\cos^2\theta\right)^{\frac{1}{2}}$

 $K_z = 2\pi/\lambda (\sin\alpha_f + \sin\alpha_i)$

For Nearest Neighbour (NN) Tilts

Tilt Angle = $\tau = tan^{-1} (K_{dz}/[K_{dxy}^2 - (K_{nxy}/2)^2]^{\frac{1}{2}})$

For Next Nearest Neighbour Tilts

 $\tau = tan^{-1} \left(K_{nz} / K_{nxy} \right)$

$\begin{aligned} \mathbf{In-plane peaks} \\ F_{hkl} &= \sum_{j} f_{j} e^{2\pi i (hx_{j} + ky_{j} + lz_{j})} \\ \frac{1}{d_{hk}^{2}} &= \frac{1}{\sin^{2} \gamma} \left(\frac{h^{2}}{a^{2}} + \frac{k^{2}}{b^{2}} - \frac{2hk}{ab} \cos \gamma \right) \\ \vec{b^{*}} &= \frac{\hat{n} \times \vec{a}}{\vec{a} \cdot \vec{b} \times \hat{n}}, \end{aligned}$

Bragg rods

$$F(\vec{K}) = \left| \int_{-\frac{L}{2}}^{\frac{L}{2}} e^{-ix\vec{K}\cdot\hat{L}} dx \right|^2 = \frac{\sin\frac{1}{2}\vec{K}\cdot L\hat{L}}{\frac{1}{2}\vec{K}\cdot L\hat{L}}$$

Langmuir Monolayers in Reciprocal Space



Very Briefly on Synchrotron Radiation



causes them to produce electromagnetic radiation In the lab rest frame, this produces a **horizontal fan of xrays that is highly collimated** in the vertical direction and extends to high energies

Synchrotron x-rays are:

- 1. Highly Collimated hence Very Bright
- 2. Linearly Polarized in the Horizontal Plane
- 3. Energy Tunable

Electrons moving near speed of light





System: Heneicosanoic Acid on water, pH changed by NaOH, no buffer

High pH behaves like High Temperature

Datta, A.; Kmetko, J.; Richter, A. G.; Yu, C. J.; Dutta, P.; Chung, K. S.; Bai, J. M. Langmuir 2000, 16, 1239.

Putting Different Metal Ions in Water: Cadmium Ions



Superlattice peaks

A superlattice of metal ions(?) is formed under the organic layer Datta, A.; Kmetko, J.; Yu, C. J.; Richter, A. G.; Chung, K. S.; Bai, J. M.; Dutta, P. J. Phys. Chem. B 2000, 104, 5797.

Cadmium Ions: the pH 'Window'





Putting Different Metal Ions in Water: Lead Ions



Are there Lead Ions in the superlattice?

organic molecules
 inorganic superlattice

 $\begin{pmatrix} \mathbf{a}' \\ \mathbf{b}' \end{pmatrix} = \begin{pmatrix} 4 & 2 \\ \overline{3} & 2 \end{pmatrix} \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \end{pmatrix}$

GID of monolayer just above and below L3 absorption edge of lead shows no change in either organic or superlattice peaks!

Lead forms less than 20% (atom%) of the superlattice



Kmetko, J.; Datta, A.; Evmenenko, G.; Durbin, M. K.; Richter, A. G.; Dutta, P. Langmuir 2001, 17, 4697.

Putting Different Metal Ions in Water



Do not form Superlattices

Form Superlattices but no chiral distortion of organic lattice

Summary



Kmetko, J.; Datta, A.; Evmenenko, G.; Dutta, P. J. Phys. Chem. B 2001, 105, 10818.

Conclusions

Metal ions can do three things to a fatty acid Langmuir Monolayer. They can:

1. Take the monolayer to a high pressure phase at low pressure i.e., an Achiral structure. Cu, Ni, Ca, Ba, Zn

2. Take the monolayer to a high pressure phase and create a superlattice underneath i.e., Achiral + Superlattice. Mg, Mn

3. Take the monolayer to a new chiral phase and create a superlattice underneath i.e., Chiral + Superlattice. Cd, Pb

Who are we?



My Colleagues

Professor M.K. Sanyal, SINP
Professor Pulak Dutta, Northwestern University, USA
Professor Jean Daillant, SOLEIL Synchrotron, France
Professor Stefano Nannarone, University of Modena and Elettra Synchrotron, Italy
Professor Ullrich Pietsch, University of Siegen, Germany

My Students (Past and Present)

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THANK YOU