Preparation of XAFS Samples

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- Firouzeh Tannazi (IIT/BCPS) (results on fluorescence in complex materials)

- Suggested References:

  - Steve Heald's article "designing an EXAFS experiment" in Koningsberger and Prins and early work cited therein

  - Rob Scarrow's notes posted at http://cars9.uchicago.edu/xafs/NSLS_2002/

  - *New book, "Introduction to XAFS", in press 2009, G. Bunker, Cambridge University Press*

Sample prep - so what?

- If you want to get correct answers with XAFS, you have to pay attention to a few things at the very beginning.

- Even nowadays the literature is rife with data that suffer from unrecognized problems that should have been avoided.

- It's much easier to prevent the problems than to try to fix them afterward. Especially when you find out your thesis data is broken.

types of samples

- solids

  - powders

  - heterogeneous collections of particles

  - films

  - lumps

- solutions

- gases

- XAFS vs temperature, pressure, pH, applied fields ...

Safety issues

- Before preparing samples, check the MSDS's for the materials you are using.

- Most samples must be encapsulated in a manner that is consistent with their physical form and degree of hazard.

Experimental Modes

- Modes:

  - Transmission

  - Fluorescence

  - Electron yield

- Designing the experiment requires an understanding of sample preparation methods, experimental modes, and data analysis

Transmission

- Simplest XAFS measurement

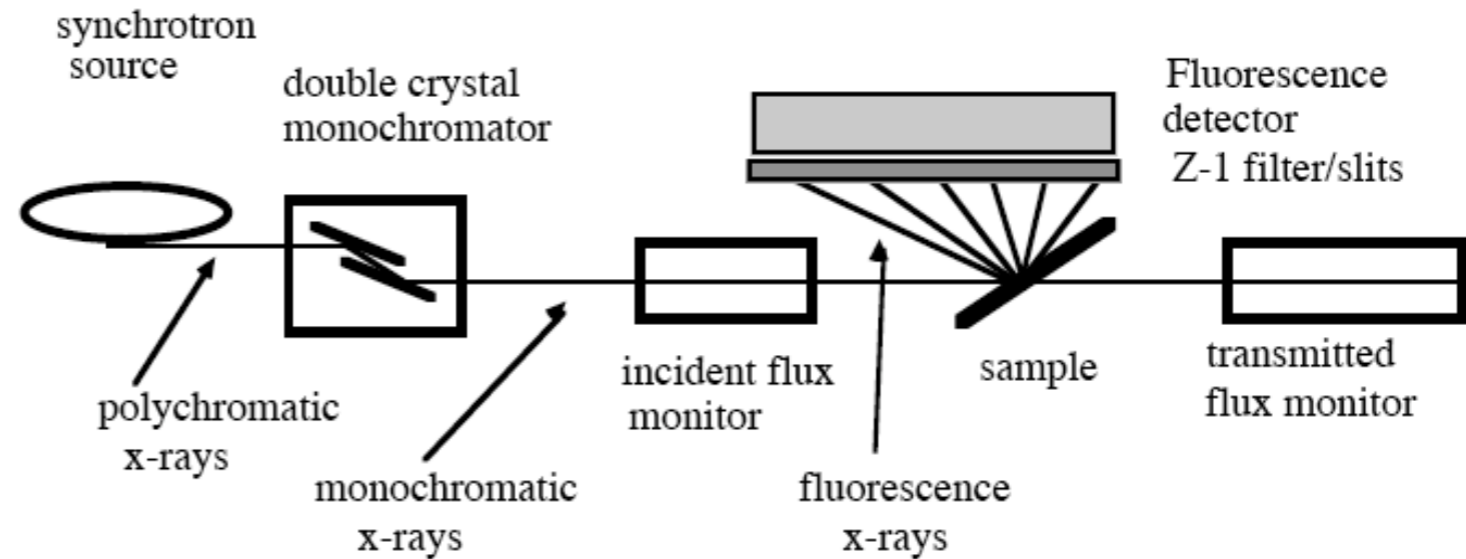- Measure relative x-ray flux transmitted through homogeneous sample

Figure 1 – Schematic XAFS experiment

which mode to use?

- If you can readily get x-rays through the sample + substrate (and the edge step is > 0.1), use transmission, otherwise use fluorescence or electron yield.

- If the sample is dilute, use fluorescence.
  If it is not dilute, the data may be distorted and fluorescence corrections may be needed. Alternatively use electron yield detection.

- Even if the sample is dilute on average, you have to deal with particle size issues.

- more on this later ...

potential pitfalls

- thickness effects in transmission

- fluorescence self-absorption

- particle size

transmission: uniform sample

Uniform, homogeneous sample:

$$\frac{I}{I_0} = \exp(-\mu(E)x)$$

x is the sample thickness

$\mu(E)$ is the linear x-ray absorption coefficient at x-ray energy E

Decreases roughly as $1/E^3$ between absorption edges

Absorption Length

$$\text{"Absorption Length"} \equiv 1/\mu$$

- It is the distance over which x-ray intensity decreases by factor 1/e ~ 37%

- *Determines the basic length scale for choosing sample thickness, particle size, and sample homogeneity*

- *Determine its value at the energy of interest when designing experiments*

Absorption Coefficient

Single substance:

$$\mu = \rho\sigma$$

ρ is the density; σ is the cross section.

If the units of ρ are g/cm^3 the cross section is in cm^2/g.

If the units of ρ are atoms/cm^3 the cross section is in cm^2/atom.

$1\text{barn} = 10^{-24}\text{cm}^2$.

Cross section

Interaction between a beam of particles (photons) and a target

Definition of "cross section" σ:

$$R[\frac{\text{photons}}{\text{s}}] = \Phi[\frac{\text{photons}}{\text{s}*\text{cm}^2}]*\sigma[\frac{\text{cm}^2}{\text{atom}}]*N[\text{atom}],$$

alternatively

$$R[\frac{\text{photons}}{\text{s}}] = \Phi[\frac{\text{photons}}{\text{s}*\text{cm}^2}] * \sigma[\frac{\text{cm}^2}{\text{g}}] * M[\text{g}]$$

If the atomic cross section is on a per-mass basis,
it is often called the "linear mass attenuation coefficient".

Sources of Cross Section Data

- W.H. McMaster et al. Compilation of X-ray Cross Sections. Lawrence Radiation Laboratory Report UCRL-50174, National Bureau of Standards, pub. (1969).
  http://www.csrri.iit.edu/mucal.html
  http://www.csrri.iit.edu/periodic-table.html

- J.H. Hubbell, Photon Mass Attenuation and Energy-Absorption Coefficients from 1 keV to 20 MeV, Int. J. Appl. Radiat. Isot. 33, 1269-1290 (1982)

- S. Brennan and P.L. Cowan, Rev. Sci. Instrum, vol 63, p.850 (1992).

- B. L. Henke, E. M. Gullikson, and J. C. Davis, Atomic Data and Nuclear Data Tables Vol. 54 No. 2 (1993).
  http://www-cxro.lbl.gov/optical_constants/atten2.html
  http://www-cxro.lbl.gov/optical_constants/

- C. T. Chantler, J. Phys. Chem. Ref. Data 24, 71 (1995)
  http://physics.nist.gov/PhysRefData/FFast/html/form.html

- W.T. Elam, B.Ravel, and J.R. Sieber, Radiat. Phys. Chem. v.63 (2002) pp 121-128.

mucal - online cross sections for elements

compounds

Absorption coefficient approximately given by

$$\mu \approx \sum_i \rho_i \sigma_i = \rho_{\mathsf{M}} \sum_i \frac{m_i}{M} \sigma_i = \rho_{\mathsf{N}} \sum_i \frac{n_i}{N} \sigma_i$$

where ρ_{M} is the mass density of the material as a whole, ρ_{N} is the number density of the material as a whole, and m_i/M and n_i/N are the mass fraction and number fraction of element i.

Example Calculation

Fe_3O_4 (magnetite) at 7.2 KeV;
http://www.csrri.iit.edu/periodic-table.html

density $5.2 \frac{g}{cm^3}$

MW$=3 * 55.9 \frac{g}{mol} + 4 * 16.0 \frac{g}{mol} = 231.7 \frac{g}{mol}$

$\sigma_{Fe} = 393.5 \frac{cm^2}{g}; \ M_{Fe} = 55.9 \ \frac{g}{mol};$

$f_{Fe} = 55.9/231.7 = .724;$

$\sigma_{O} = 15.0 \ \frac{cm^2}{g}; \ M_{O} = 16.0 \ \frac{g}{mol};$

$f_{O} = 16.0/231.7 = .276;$

$\mu = 5.2 \frac{g}{cm^3}(.724 * 393.5 \frac{cm^2}{g} + .276 * 15.0 \frac{cm^2}{g})$
$= 1503/cm = .15/micron$

Absorption Length $= 1\mu m/.15 = 6.7$ microns

Even if you don't know the density exactly, you can estimate it
from something similar. It's probably between 2 and 8 g/cm^3

Transmission: nonuniform sample

What's the problem with nonuniform samples?

Characterized by thickness distribution $P(x)$

$$\mu x_{\mathrm{eff}}(E) = -\ln \int_0^\infty P(x) \exp\left(-\mu(E)x\right)dx$$

$$= -\sum_{n=1}^\infty \frac{C_n(-\mu)^n}{n!},$$

where C_n are the cumulants of the thickness distribution ($C_1 = \bar{x}$, $C_2 = $ mean square width, etc.)

A Gaussian distribution of width σ has

$$\mu x_{\mathrm{eff}}(E) = \mu \bar{x} - \mu^2 \sigma^2/2$$

ref gb dissertation 1984

Effect of Gaussian thickness variation

$$P(x) = \frac{1}{\sigma\sqrt{(2\pi)}} \exp\left(\frac{-(x-\bar{x})^2}{2\sigma^2}\right)$$

$P(x)$	μx_{eff} and $\mu\bar{x}$ vs μ	$\mu x_{\text{eff}}'$ vs μ

$\sigma = 0.1$

$\sigma = 0.3$
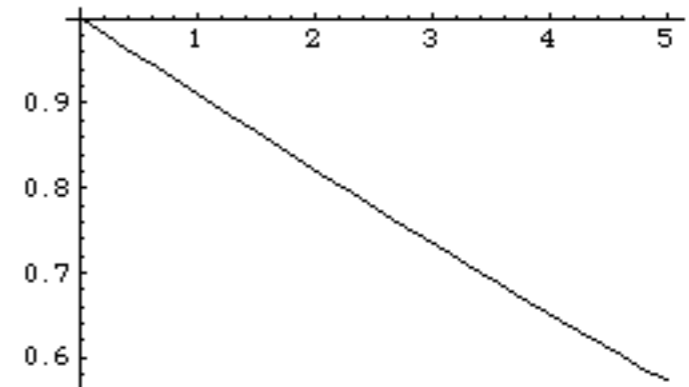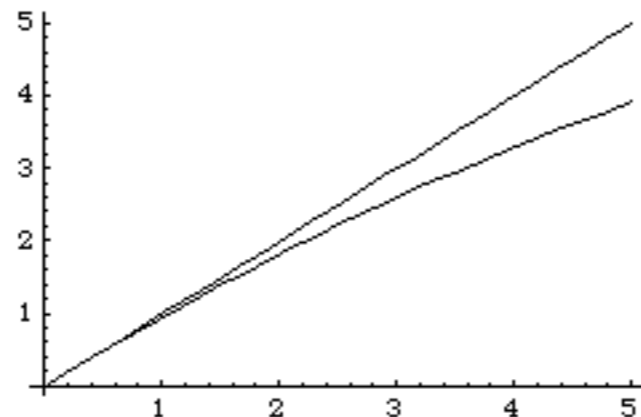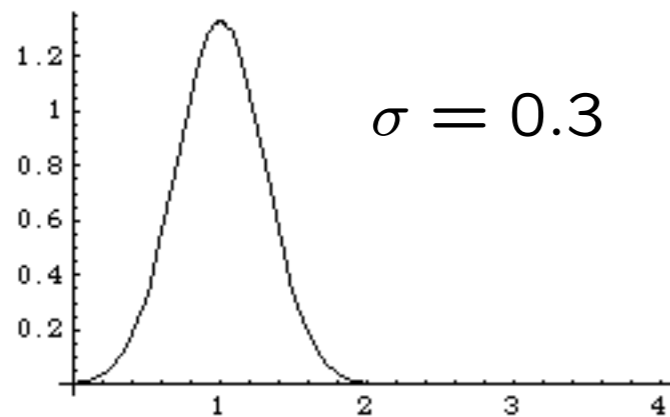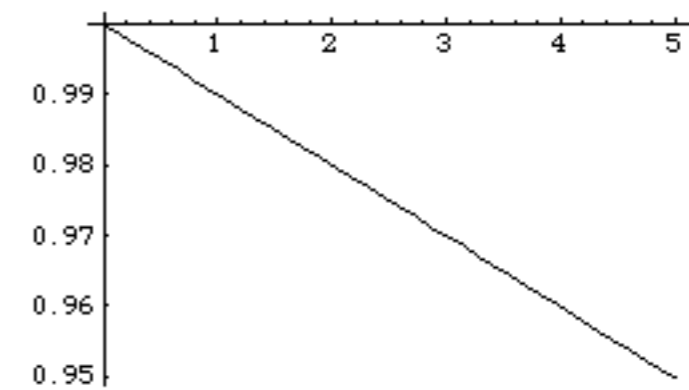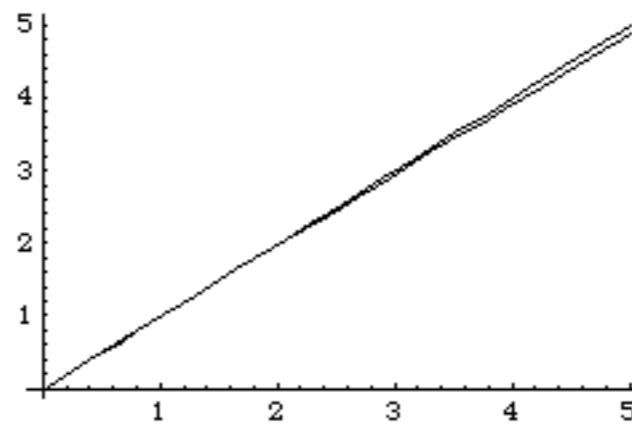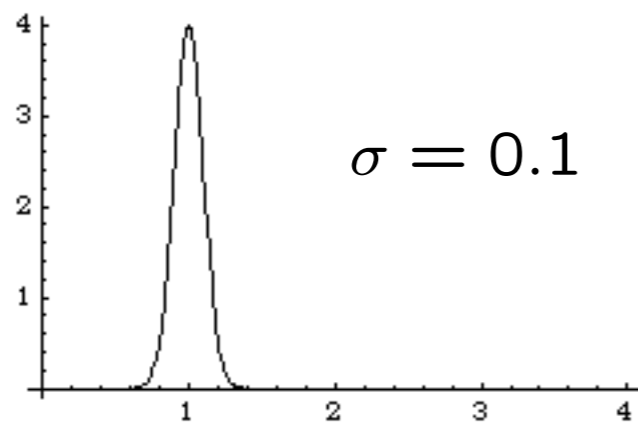
Effect of leakage/harmonics

Leakage (zero thickness) fraction a, together with gaussian variation in thickness centered on x_0 with width σ:

$$P(x) = a\delta(x) + (1-a)\frac{1}{\sigma\sqrt{2\pi}}\exp\left(\frac{-(x-\bar{x})^2}{2\sigma^2}\right)$$

$$\mu x_{\mathsf{eff}}(E) = -\ln\left(a + (1-a)\exp\left(-\mu x_0 + \mu^2\sigma^2/2\right)\right)$$
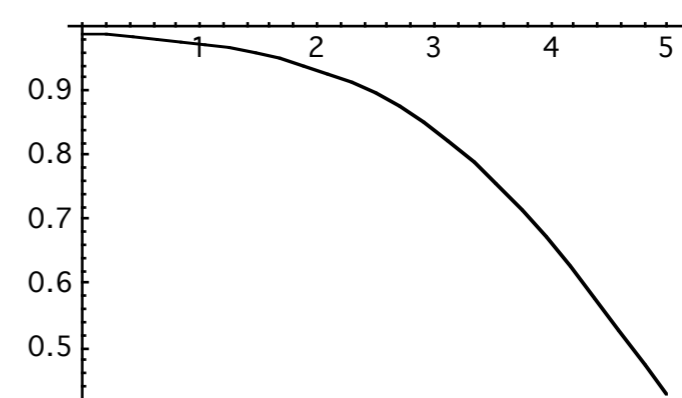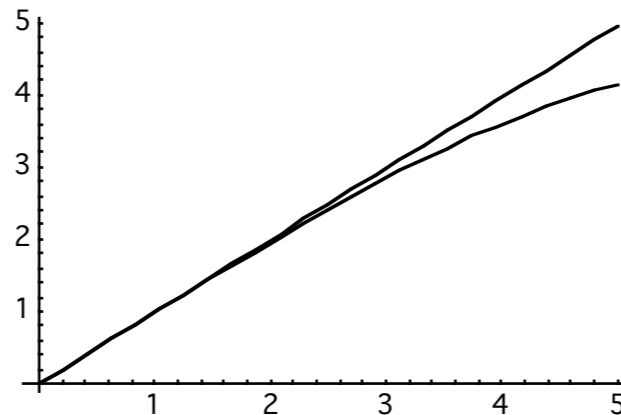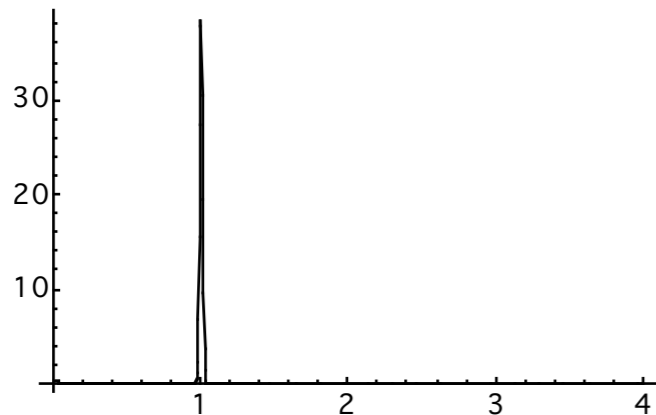
Example - Layers of spheres
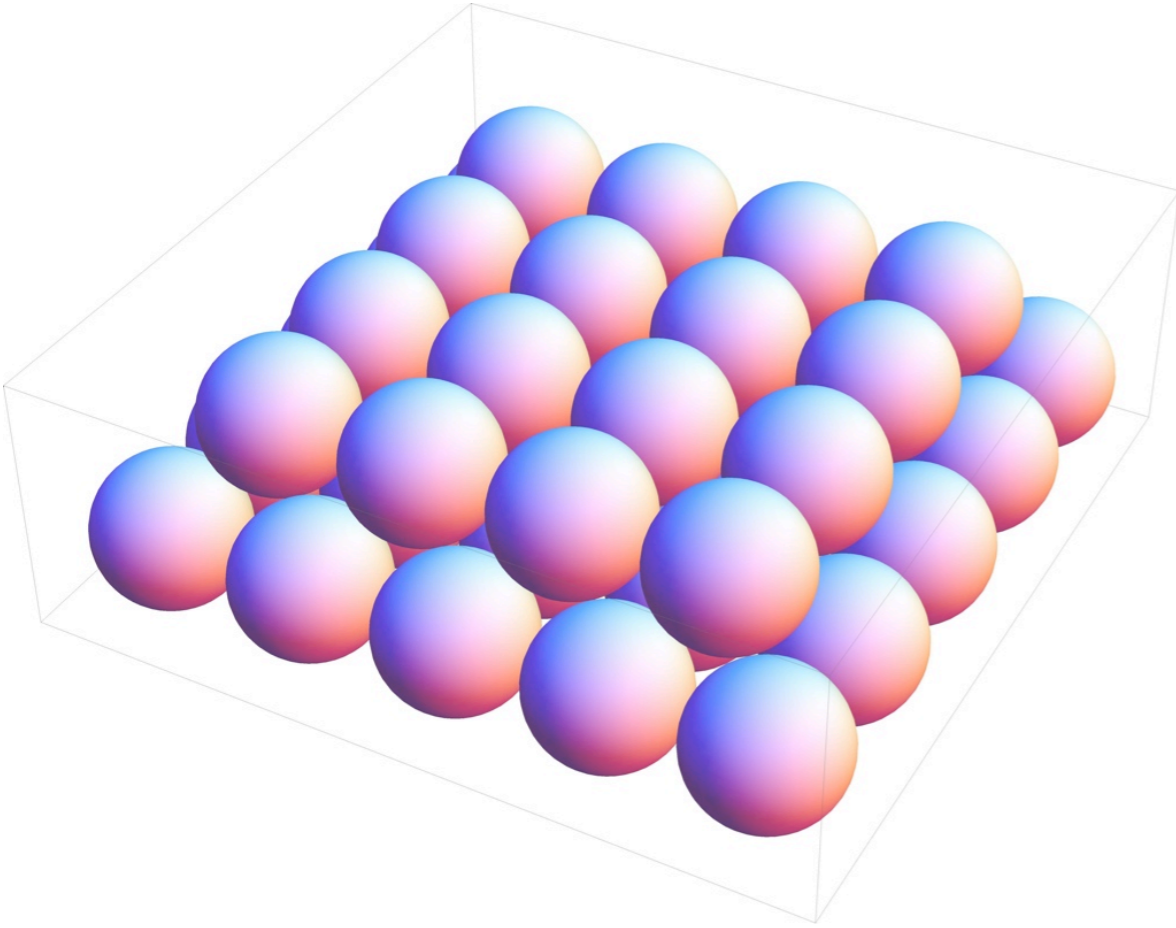
Layers of spheres
stacked (no holes)

Thickness
Distribution
is broad →
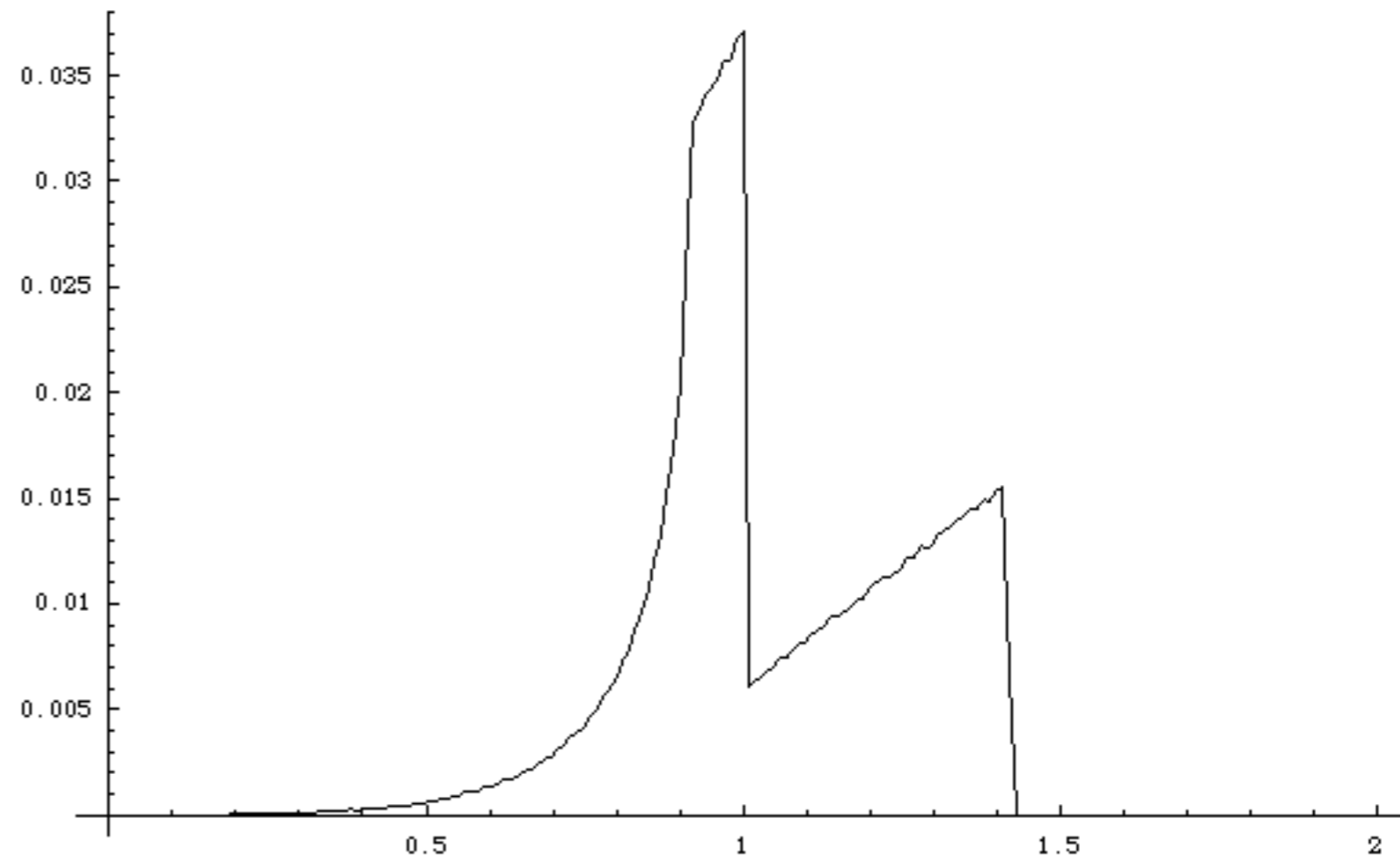
Effect of pinholes (leakage) or harmonics

$$P(x) = a\delta(x) + (1-a)\frac{1}{\sigma\sqrt{2\pi}}\exp\left(\frac{-(x-\bar{x})^2}{2\sigma^2}\right)$$

$P(x)$	μx_{eff} and $\mu\bar{x}$ vs μ	$\mu x_{\text{eff}}'$ vs μ

$a = .02$

$a = .05$
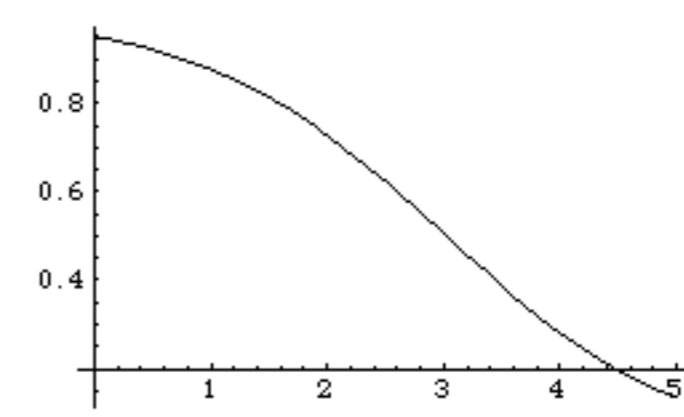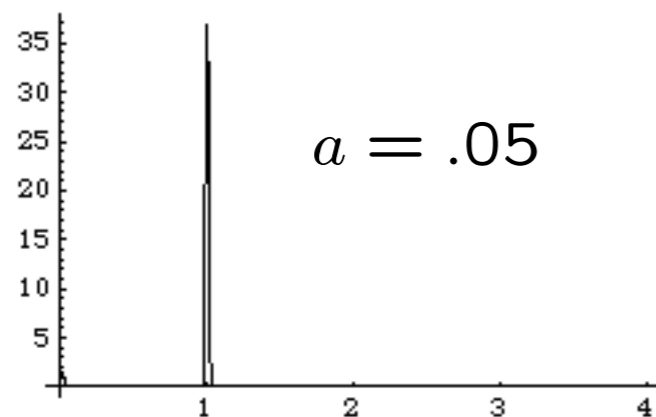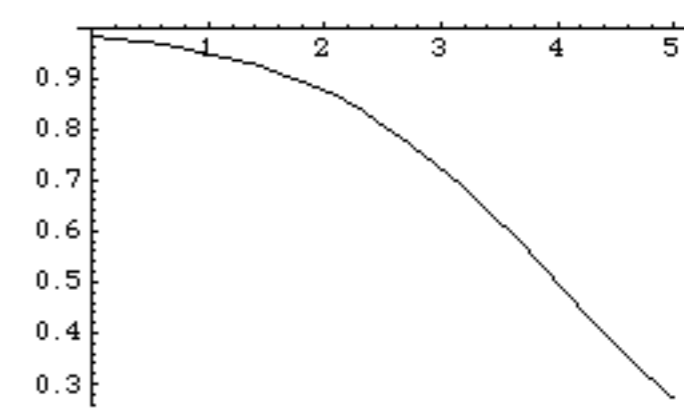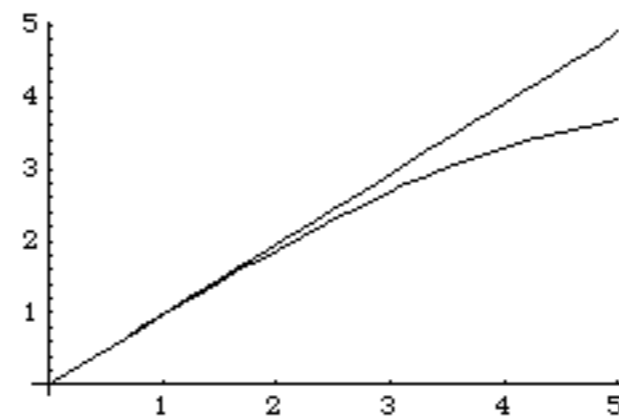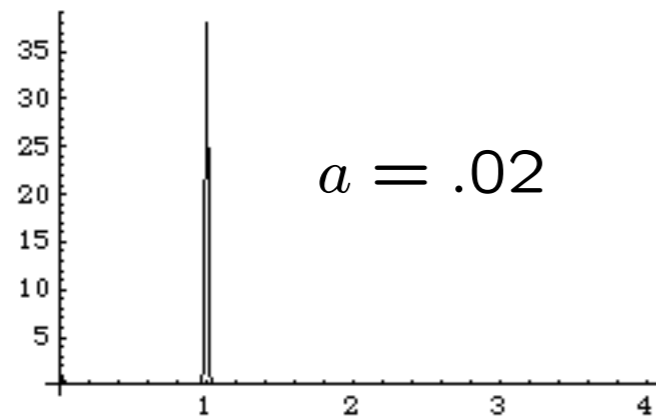
Effect of Leakage on spectra

- MnO 10 micron thick
- ~2 absorption lengths

- leakage varied from 0% to 10%

- Edge jump is reduced

- EXAFS amplitudes are reduced

- white line height compressed

- thickness effects distort both XANES and EXAFS - screw up fits and integrals of peak areas

- If you are fitting XANES spectra, watch out for these distortions
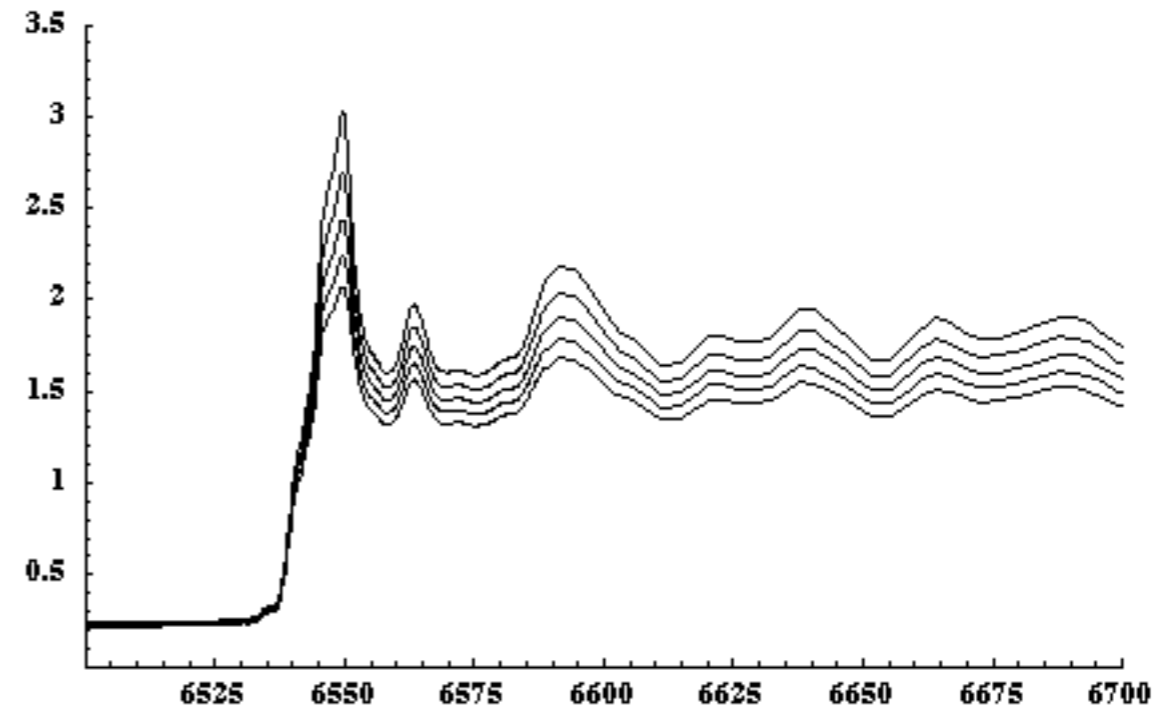
Thickness effects always reduce EXAFS Amplitudes

The measured EXAFS is the variation in apparent absorption $f(\mu)$ above the edge, divided by the measured edge step:

$$\chi_{eff} = \frac{f(\mu_a+\delta\mu)-f(\mu_a)}{f(\mu_a)-f(\mu_b)} \sim \frac{df}{d\mu}\bigg|_{\mu a} \frac{\delta\mu}{f(\mu_a)-f(\mu_b)}$$

where $\delta\mu$ is the true variation in μ (which us taken to be small), and μ_a and μ_b are respectively the absorption above and below the

edge. The true χ is defined as $\chi = \frac{(\mu_a+\delta\mu)-(\mu_a)}{\mu_a-\mu_b} = \frac{\delta\mu}{\mu_a-\mu_b}$. Thus, thickness effects alter

the measured EXAFS amplitudes by the ratio: $\frac{\chi_{eff}}{\chi} = \frac{df}{d\mu}\bigg|_{\mu a} \frac{\mu_a-\mu_b}{f(\mu_a)-f(\mu_b)}$. To evaluate the

right side of this equation, consider the taylor expansion:

$$f(\mu_b) = f(\mu_a) + \frac{df}{d\mu}\bigg|_{\mu a} (\mu_b - \mu_a) + \frac{1}{2}\frac{d^2f}{d\mu^2}\bigg|_{\mu a} (\mu_b - \mu_a)^2 + \dots.$$

This can be rewritten:

$$\frac{df}{d\mu}\bigg|_{\mu a} - \frac{f(\mu_a)-f(\mu_b)}{(\mu_a - \mu_b)} = \frac{1}{2}\frac{d^2f}{d\mu^2}\bigg|_{\mu a} (\mu_a - \mu_b) + \dots.$$

The series is essentially an expansion in powers of a parameter of size roughly $\sim\mu_a\sigma$, where σ is the rms width of P(x). From the previous discussion, the curvature of f is always negative or zero, and $\mu_a>\mu_b$, which implies that right side is negative or zero. Therefore χ_{eff}/χ is less than (or at most equal to) unity.

from   http://gbxafs.iit.edu/training/thickness_effects.pdf

Simple model of thickness distribution

Thickness distribution is a sum of gaussians of weight a_n, thickness x_n, and width σ_n:

$$P(x) = \sum_n \frac{a_n}{\sigma_n \sqrt{2\pi}} \exp\left(\frac{-(x - x_n)^2}{2\sigma_n^2}\right)$$

$$\mu x_{\mathsf{eff}}(E) = -\ln\left(\sum_n a_n \exp\left(-\mu x_n + \mu^2 \sigma_n^2 / 2\right)\right)$$

This expression can be used to estimate the effect of thickness variations

Transmission -Summary

- Samples should be made uniform on a scale determined by the absorption length of the material

- Absorption length should be calculated when you're designing experiments and preparing samples

When to choose Transmission

- You need to get x-rays through the sample

  - Total thickness should be kept below <2-3 absorption lengths including substrates to minimize thickness effects

    - "beam hardening" - choose fill-gases of back ion chamber to minimize absorption of harmonics; get rid of harmonics by monochromator detuning, harmonic rejection mirrors, etc.

  - Element of interest must be concentrated enough to get a decent edge jump (> 0.1 absorption length)

  - Pinholes and large thickness variations should be minimized

  - If you can't make a good transmission sample, consider using fluorescence or electron yield

Fluorescence Radiation in the Homogeneous Slab Model

- Probability the photon penetrates to a depth x in the sample

- and that is absorbed by the element i in a layer of thickness dx

- and as a consequence it emits with probability ε a fluorescence photon of energy E_f

- which escapes the sample and is radiated into the detector

I_0　　　　　　　　　I_f

θ　　ϕ

x
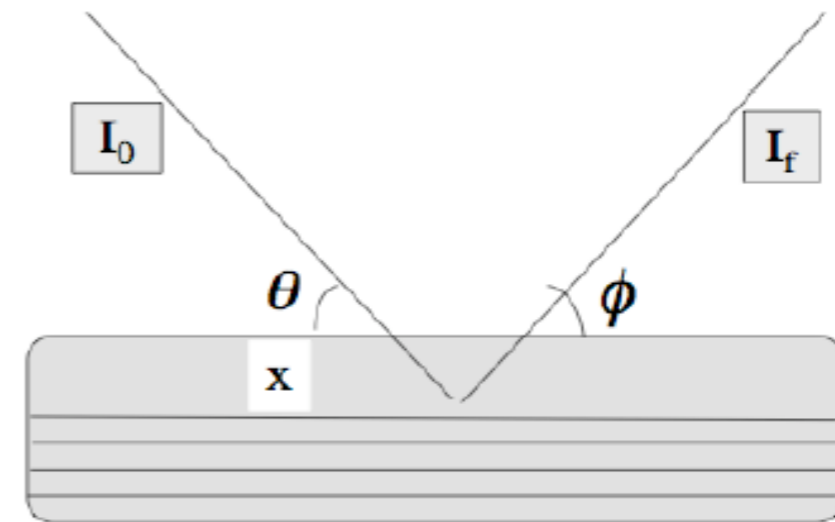
- Thin Sample

$$dI_f = I_0 \epsilon_a \frac{\mu_a(E)}{\sin\theta} e^{\frac{-\mu(E)x}{\sin\theta}} e^{\frac{-\mu(E_f)x}{\sin\Phi}} dx$$

$$[(\frac{\mu_T}{\sin\theta} + \frac{\mu_f}{\sin\phi})d] \ll 1$$

$$I_f = \frac{I_0\epsilon_a(\frac{\mu_a}{\sin\theta})}{\frac{\mu_T}{\sin\theta} + \frac{\mu_f}{\sin\phi}} [1 - e^{-(\frac{\mu_T}{\sin\theta} + \frac{\mu_f}{\sin\phi})d}].$$

$$(I_f)_{thin} = I_0\epsilon_a(\frac{\mu_a}{\sin\theta})\, d$$

Fluorescence samples

- Thin concentrated limit is simple

- Thick dilute limit is simple

- Thick concentrated requires numerical corrections (e.g. Booth and Bridges, Haskel's fluo). Thickness effects can be corrected also if necessary by regularization (Babanov et al).

- Sample Requirements

  - Particle size must be small compared to absorption lengths of particles (not just sample average)

    - Can be troublesome for in situ studies

  - Homogeneous distribution

  - Flat sample surface preferred

Speciation problems

Nonlinear distortions of the spectra depend on particle size and distribution. This affects speciation results

Fluorescence vs Particle Size
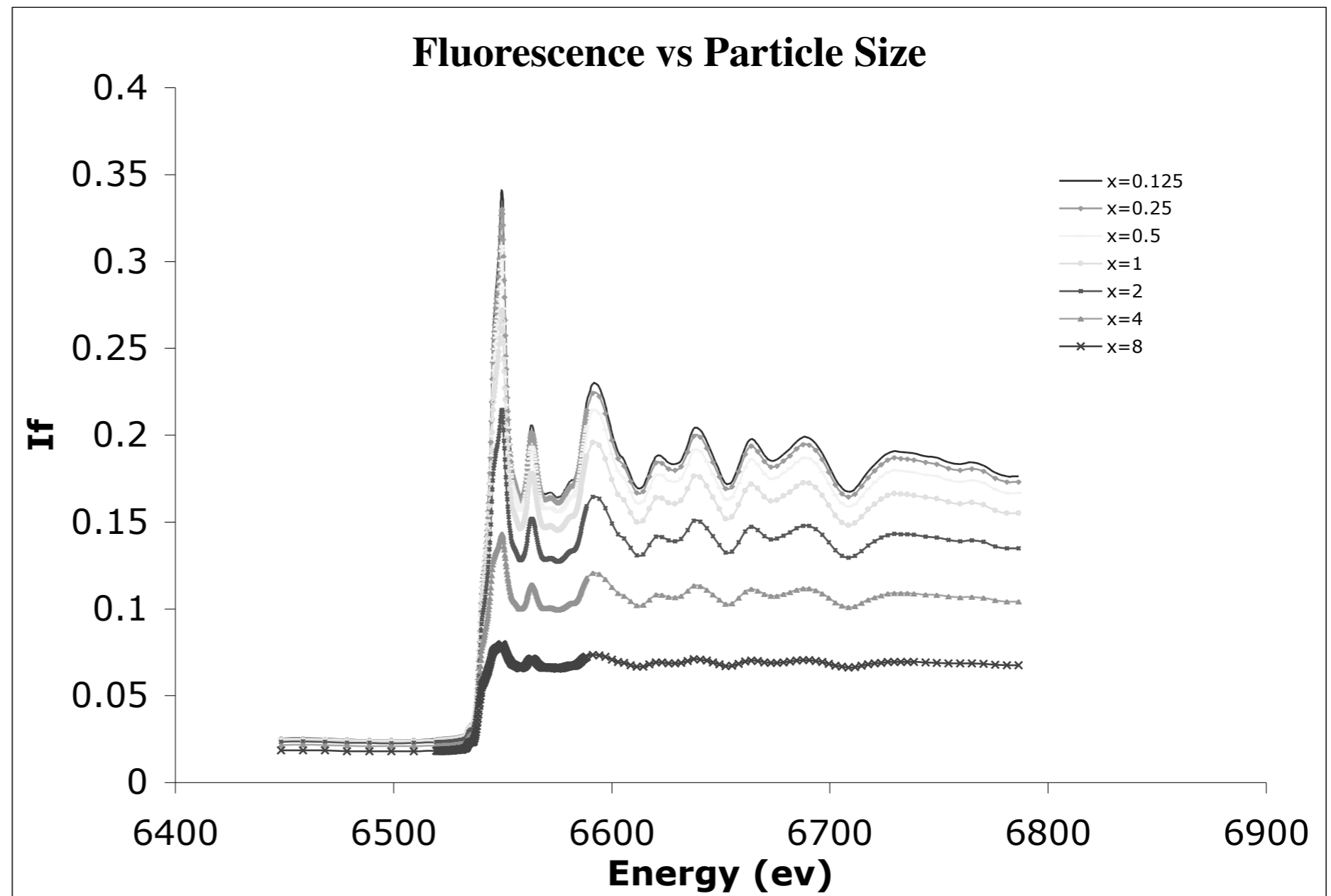
Modeling Fluorescence

- Monte Carlo and analytical calculations of Tannazi and Bunker

- Analytical calculations build on work by Hunter and Rhodes, and Berry, Furuta and Rhodes (1972)

$$\hat{n}_0 = \sin\theta_0 \, \cos\phi_0 \, \hat{i} + \sin\theta_0 \, \sin\phi_0 \, \hat{j} + \cos\theta_0 \, \hat{k},$$

$$\hat{n}_1 = \sin\theta_1 \, \cos\phi_1 \, \hat{i} + \sin\theta_1 \, \sin\phi_1 \, \hat{j} + \cos\theta_1 \, \hat{k}$$

$$P_{\vec{r}} \propto e^{-\mu d_0} e^{-\mu_f d_1},$$

$$\bar{P} = \underbrace{\frac{P_{\vec{r_1}} + P_{\vec{r_2}} + \cdots + P_{\vec{r_k}}}{k}}_{Number\ of\ the\ points\ that\ satisfy\ the\ surface\ equation}$$

Outgoing fluorescence photon direction

$\hat{n}_1$

Particle

d_1

$\vec{r}$

d_0

$\hat{n}_0$

Incoming photon direction
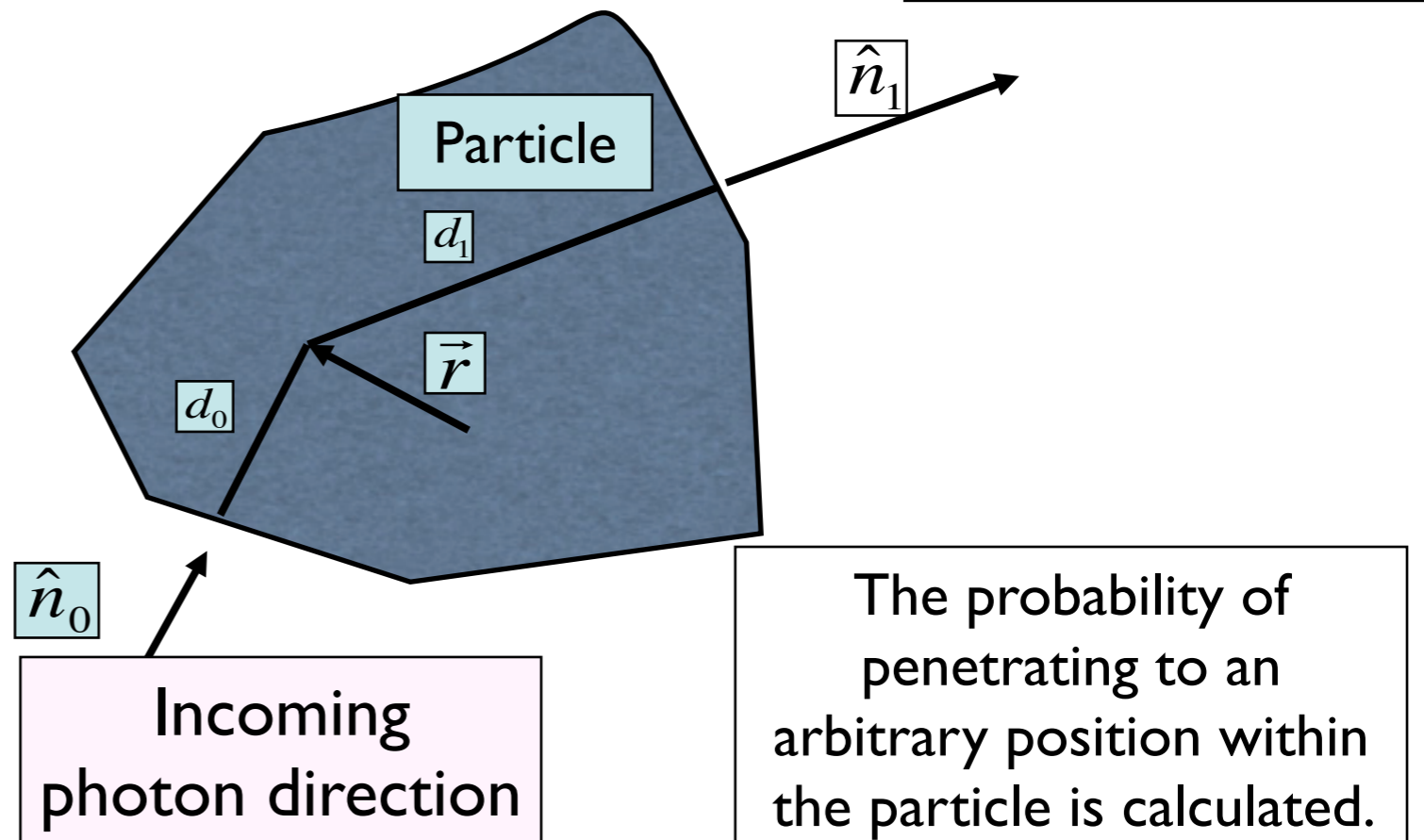
The probability of penetrating to an arbitrary position within the particle is calculated. This probability is averaged over the whole particle by Monte Carlo integration.

Cuboidal
Particles
(stereo)
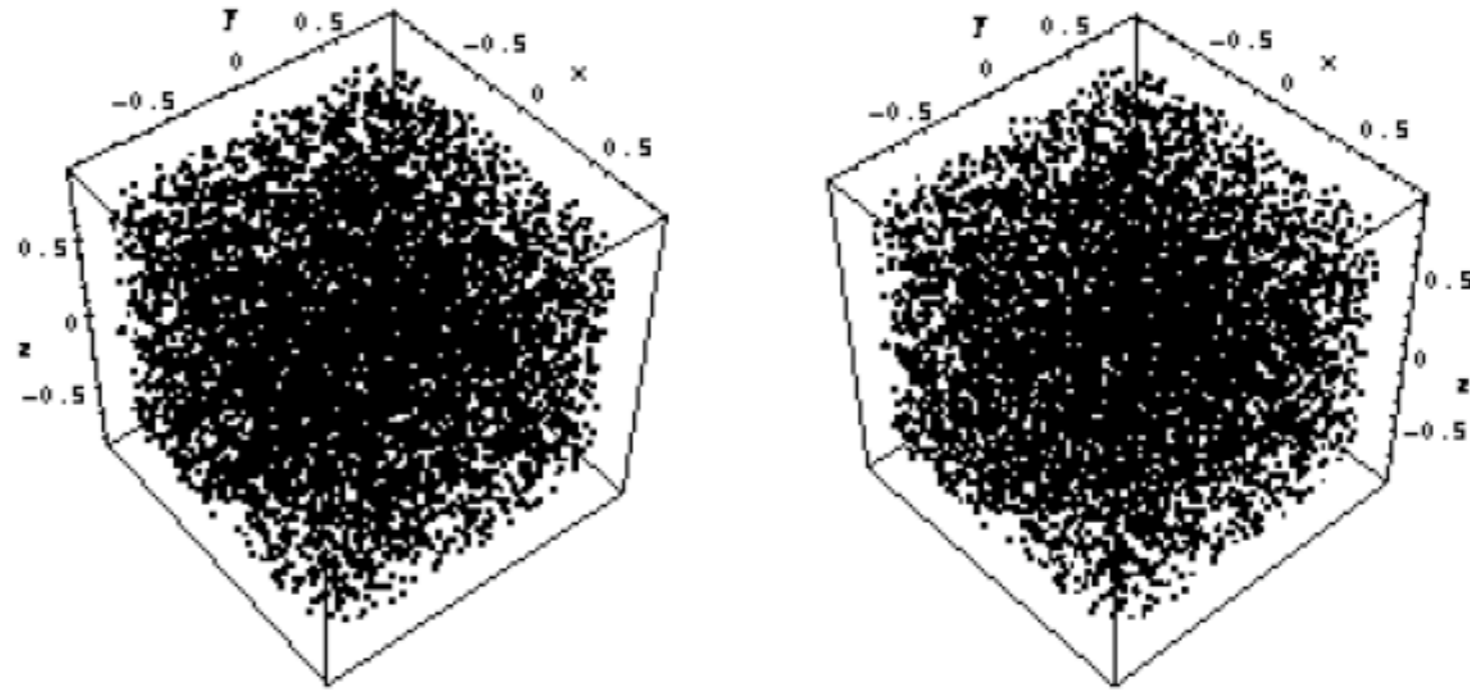
Calculate the
probability
as function
of mu and mu_f
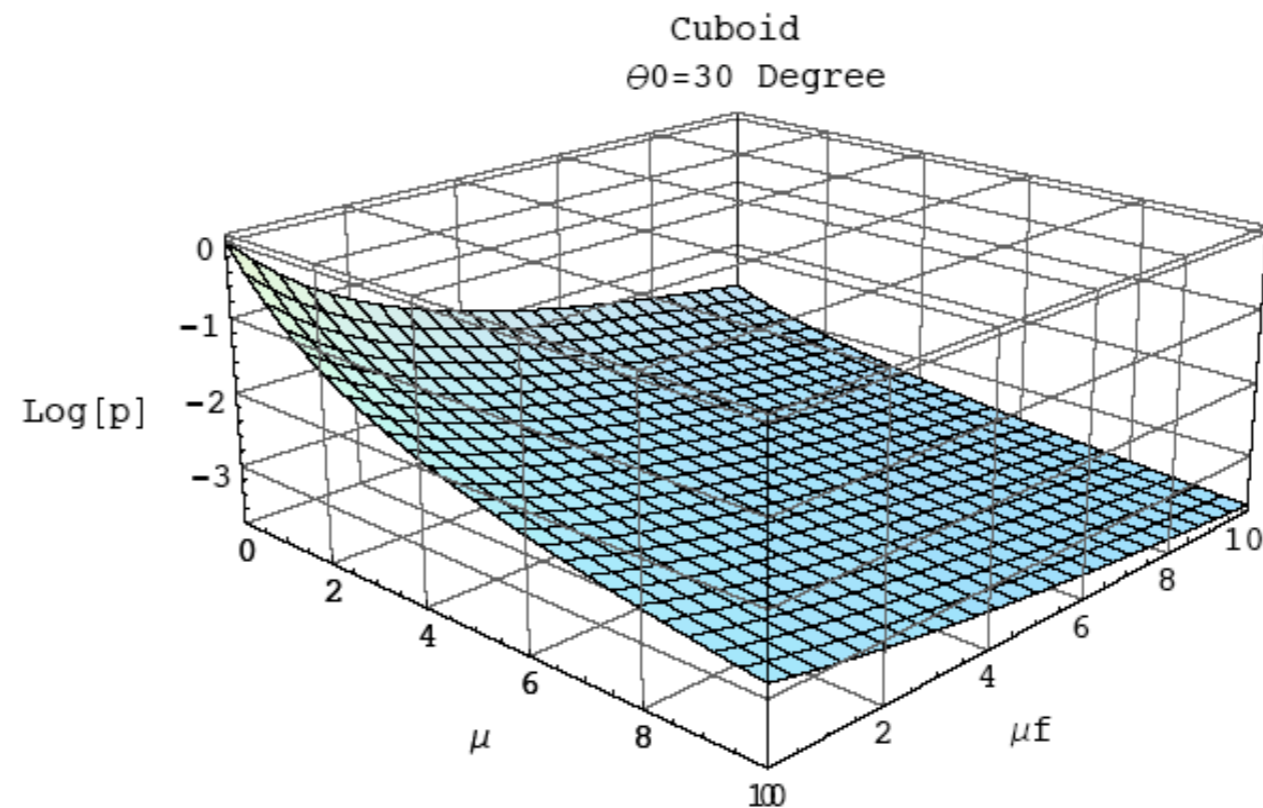
Cuboid
θ0=30 Degree

Different Orientations

d0,d1 maps →

Text
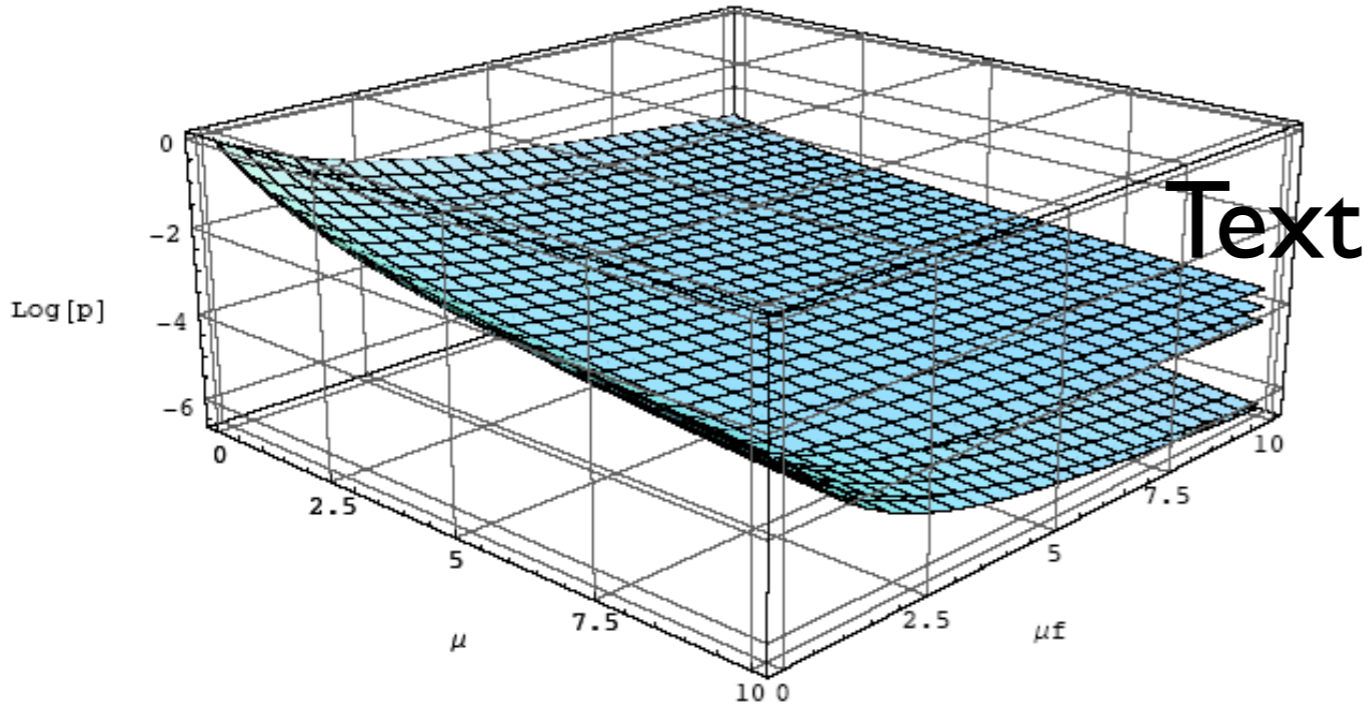
Even the particle
orientation matters
if particles too large
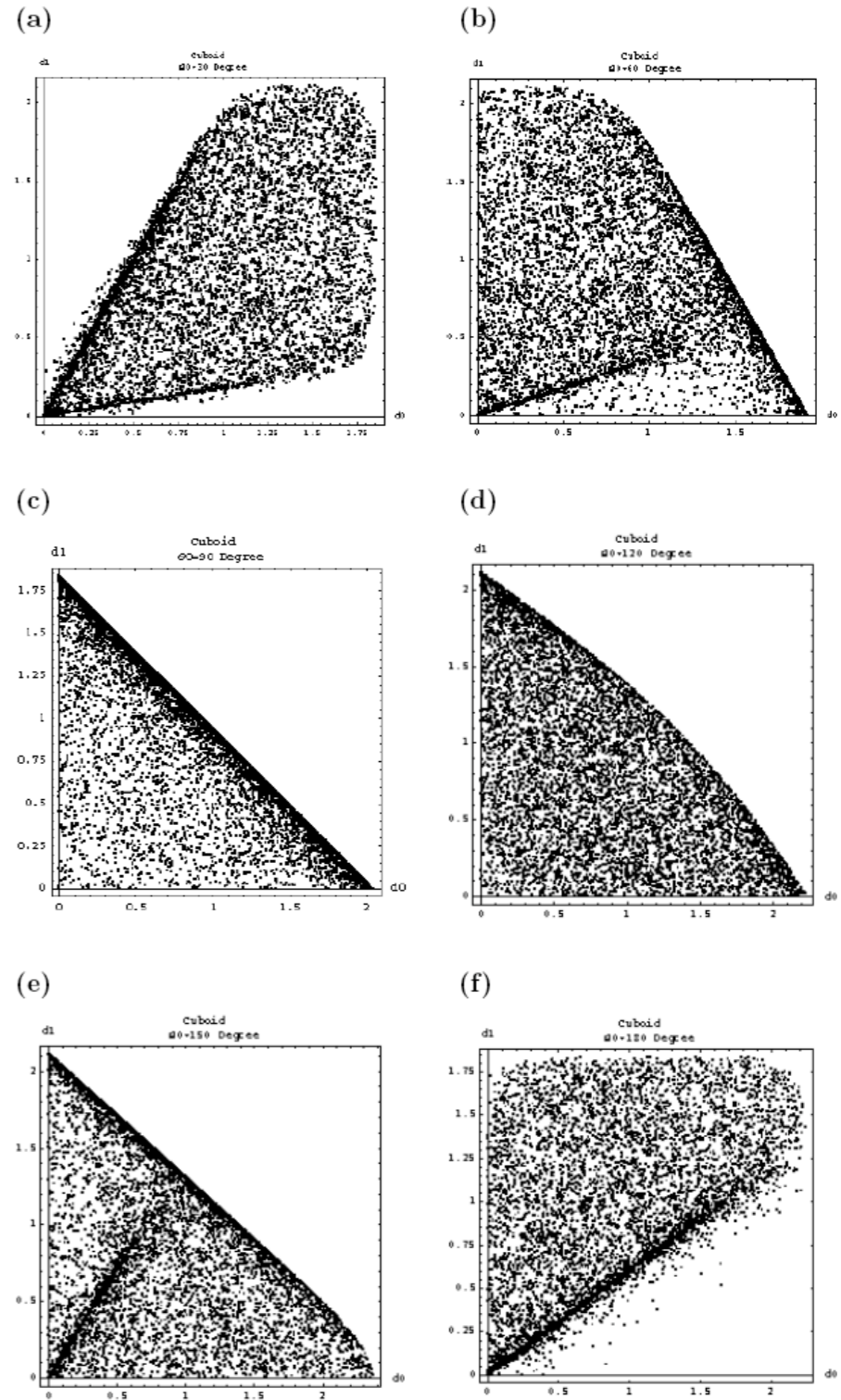
Figure 5.8. $\{d_0, d_1\}$ Maps for Cuboid at $\theta_0 =$: (a) 30, (b) 60, (c) 90, (d) 120, (e) 150, and (f) 180 degrees and $\theta_1 = \pi - \theta_0$ degrees.

$$\bar{P} = \int F(d_0, d_1) e^{-(\mu d_0 + \mu_f d_1)} dd_0 dd_1.$$

$$\log \bar{P} = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{(\mu)^n}{n!} \frac{(\mu_f)^m}{m!} C_{nm}$$
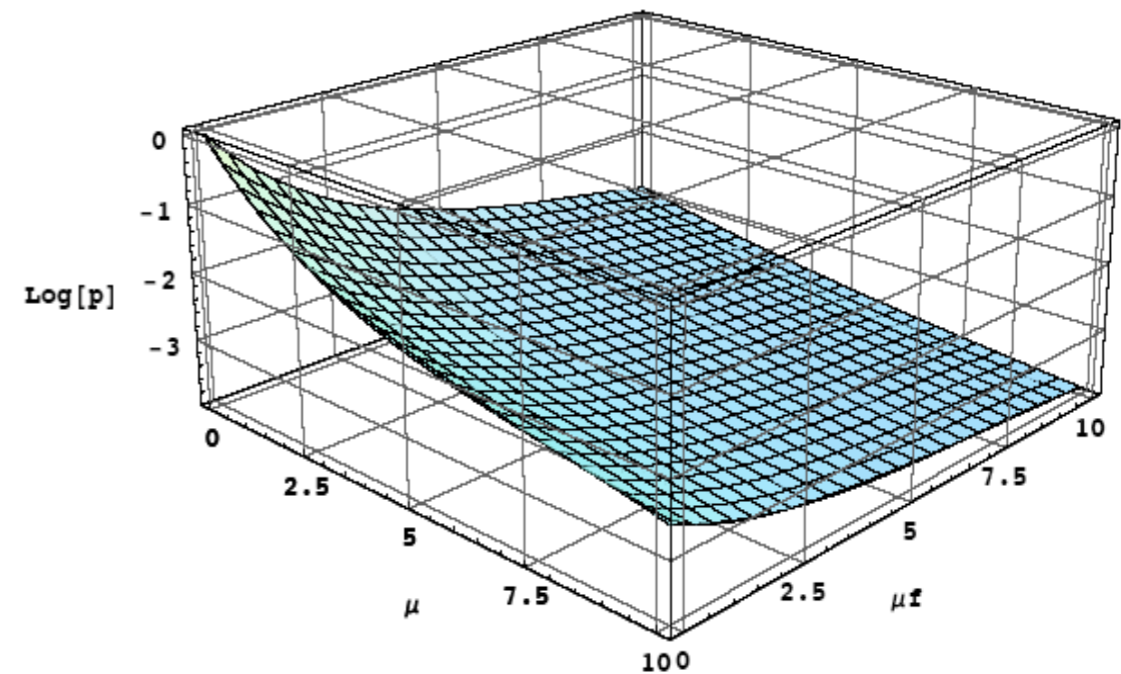
- The log of the mean probability can be expanded as a power series in both μ and μ_f. The coefficients are related to the cumulants of the (2D) distribution of distances d0,d1. The main point is that the probabilities for a given shape of particle (and theta, phi) can be parameterized by a handful of numbers, the coefficients.

Figure 5.11. Sphere

Other shapes tabulated in Firouzeh Tannazi dissertation

easily calculated for any convex particle shape
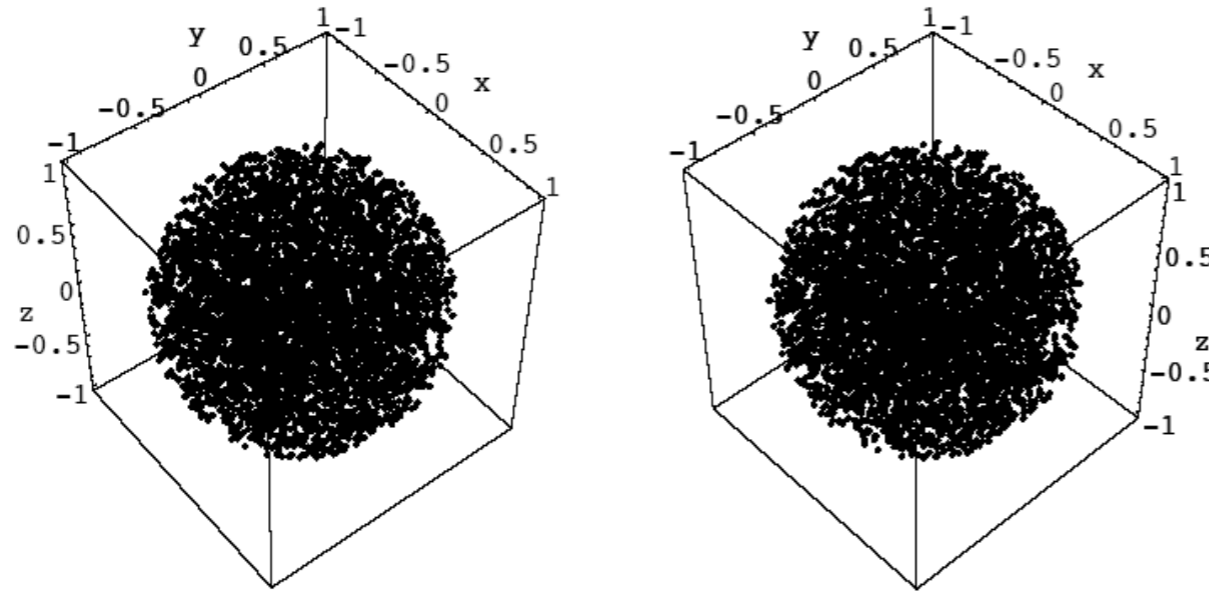
Table 5.3. Cumulant Coefficients Table for Sphere

$Coef.$	$\theta_0 = 30°$	$\theta_0 = 60°$	$\theta_0 = 90°$	$\theta_0 = 120°$	$\theta_0 = 150°$	$\theta_0 = 180°$
1	-0.0509	-0.051	-0.051	-0.0499	-0.0492	-0.0501
μ	-0.6484	-0.651	-0.645	-0.6552	-0.6624	-0.6572
μ^2	0.068	0.0677	0.0673	0.06798	0.0687	0.0683
μ^3	-0.0029	-0.003	-0.0029	-0.0029	-0.0029	-0.0029
$\mu\mu_f$	0.13399	0.017	-0.1328	-0.1407	0.0033	0.12685
$\mu^2\mu_f$	-0.0158	0.0011	0.0173	0.0187	0.0034	-0.01459
$\mu^3\mu_f$	0.0007	-0.0001	-0.0008	-0.0008	-0.00023	0.00062
$\mu\mu_f^2$	-0.016	0.0018	0.0168	0.01783	0.0029	-0.01451
$\mu^2\mu_f^2$	0.0019	-0.0006	-0.0019	-0.00202	-0.00076	0.0017
$\mu^3\mu_f^2$	-0.00008	0.00004	0.00008	0.00008	0.00004	-0.000074
$\mu\mu_f^3$	0.00068	-0.00017	-0.00074	-0.00078	-0.00021	0.00062
$\mu^2\mu_f^3$	-0.00008	0.00004	0.00008	0.000081	0.00004	-0.00007
$\mu^3\mu_f^3$	3.5×10^{-6}	-2.1×10^{-6}	-3.01×10^{-6}	-3.08×10^{-6}	-2.2×10^{-6}	3.12×10^{-6}
μ_f	-0.6521	-0.672	-0.6562	-0.6548	-0.663	-0.6468
μ_f^2	0.0678	0.07063	0.0681	0.0683	0.0689	0.0663
μ_f^3	-0.0029	-0.00301	-0.0029	-0.0029	-0.0029	-0.0028

Dilution

- Even if the sample is dilute on average you may not be really in the dilute limit

- Each fluorescent particle must be small enough, otherwise you will get distorted spectra

- Don't just mix up your particles with a filler and assume the sample is ok. Make the particles are small enough first, and calculate what "small" means.

Hunter and Rhodes Model
Continuous Size Distribution

- This model is a generalization of BFR model that has been developed by the authors above (1972), and is a formulation for continuous size distribution.

- In this approach we need to define a particle size distribution function:

$$\int_{a_{min}}^{a_{max}} f(a)\,da = 1$$

- Where a_{min} and a_{max} are the smallest and larges particle size in the sample and a is the particle size that is a variable in this approach.

- The probabilities term compare to the BFR model are defined as differential probabilities here: $P_f(a,a')\,da$.

- For calculation average transmission or fluorescence radiation through I layers we need to consider three different cases: No overlap in all layers, Some overlap and, total overlap.

- The total Fluorescence radiation is obtained from this formula, which we are adapting to XAFS.
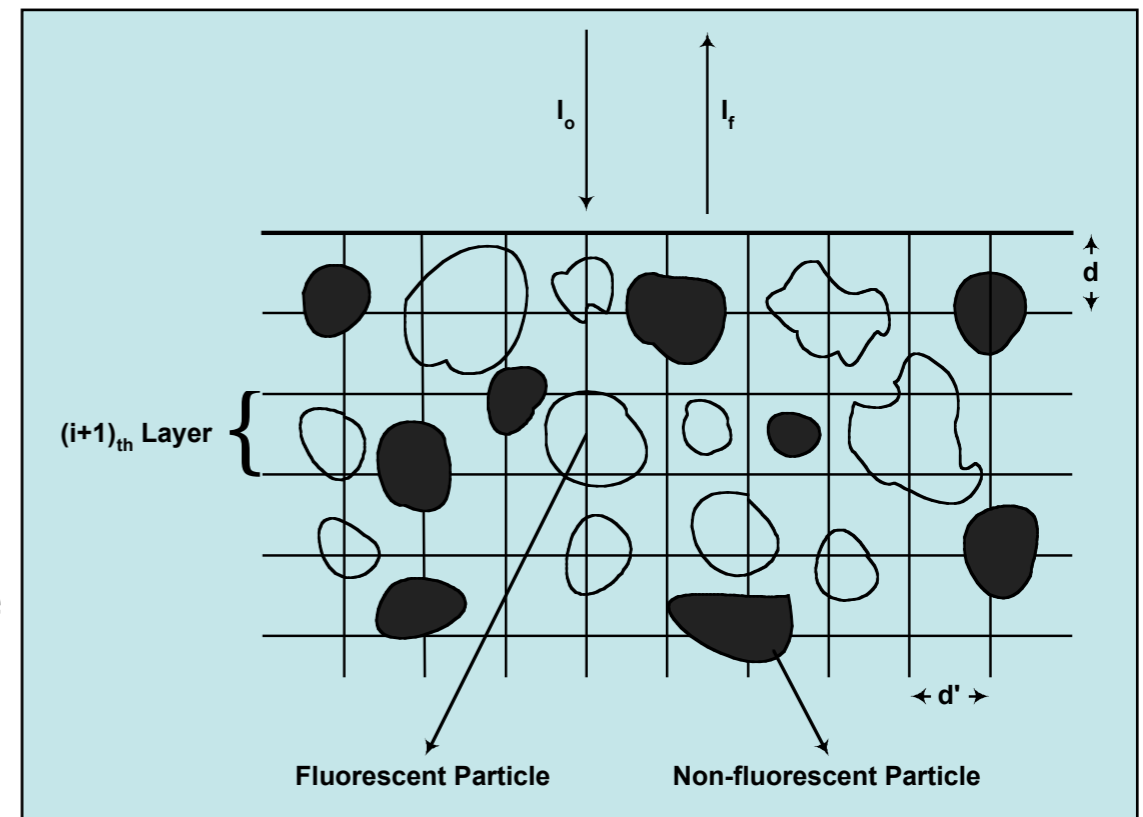
HR Model

$$dI(a)_{i+1} = \frac{I_0}{A} \cdot \bar{J}_i(a) \cdot \bar{J}_{if}(a) \cdot (dn_f(a))_a \cdot \bar{\alpha} \cdot F(a)$$

$$dI_f(a) = \frac{I_0 \epsilon_a \mu_a(E) \eta C_f f(a) [1 - e^{-\sqrt{2}(\mu_{Tf}(E) + \mu_f(E_f))a}]}{[\mu_{Tf}(E) + \mu_f(E_f)]} \times$$

$$\sum_{i=0}^{n} (\bar{J}(a) \cdot \bar{J}(a))^i$$

$$J_1(a) = 1 - a\eta \int_{a_{\min}}^{a_{\max}} \frac{1}{\bar{d}} (C_f \ f(a')[1 - e^{-\sqrt{2}\mu_{Tf}(E)\bar{d}}] +$$

$$C_n \ g(a')[1 - e^{-\sqrt{2}\mu_{Tn}(E)\bar{d}}])da'$$

HR Model

nonlinear compression of spectra

Fluorescence in HR Model
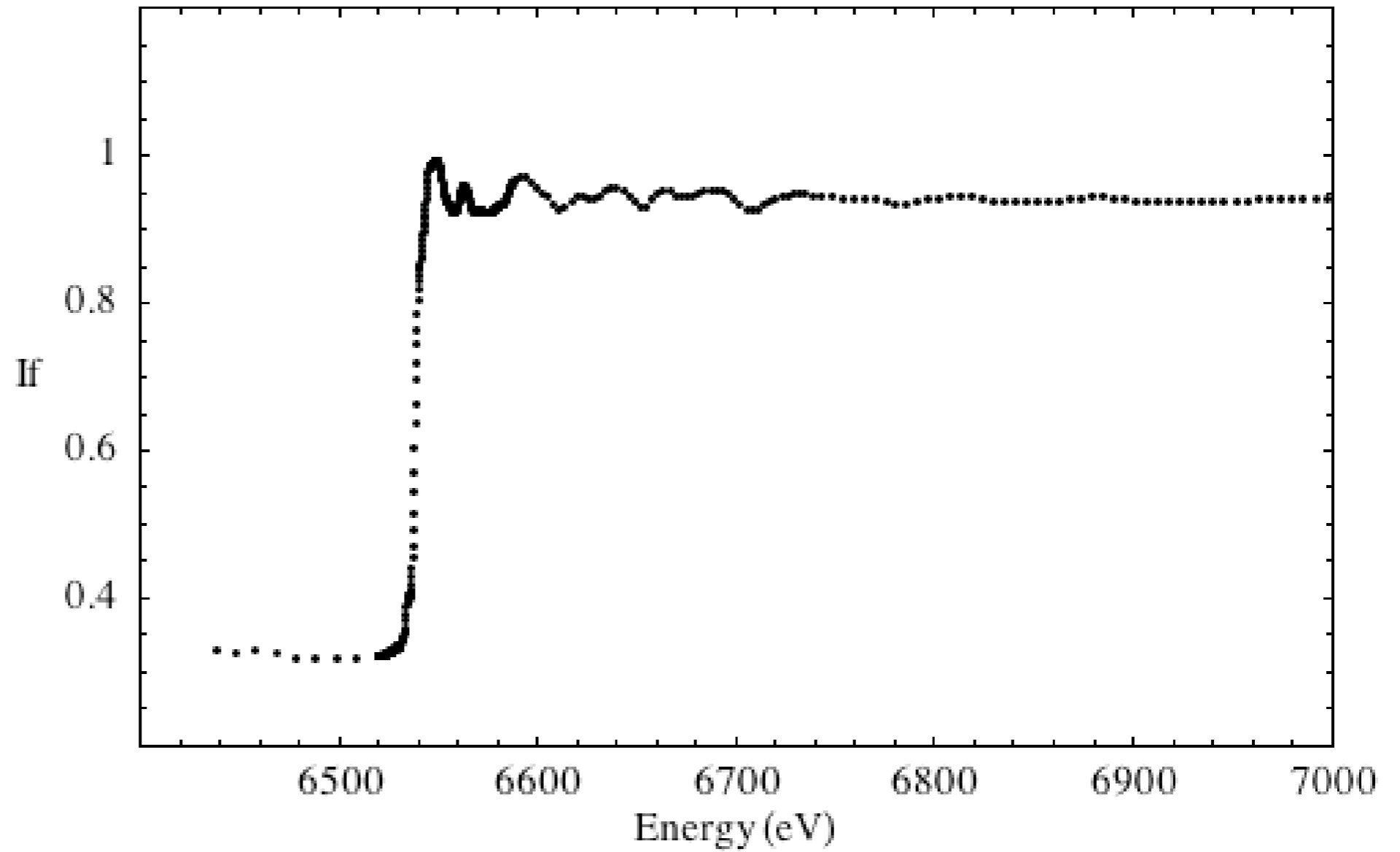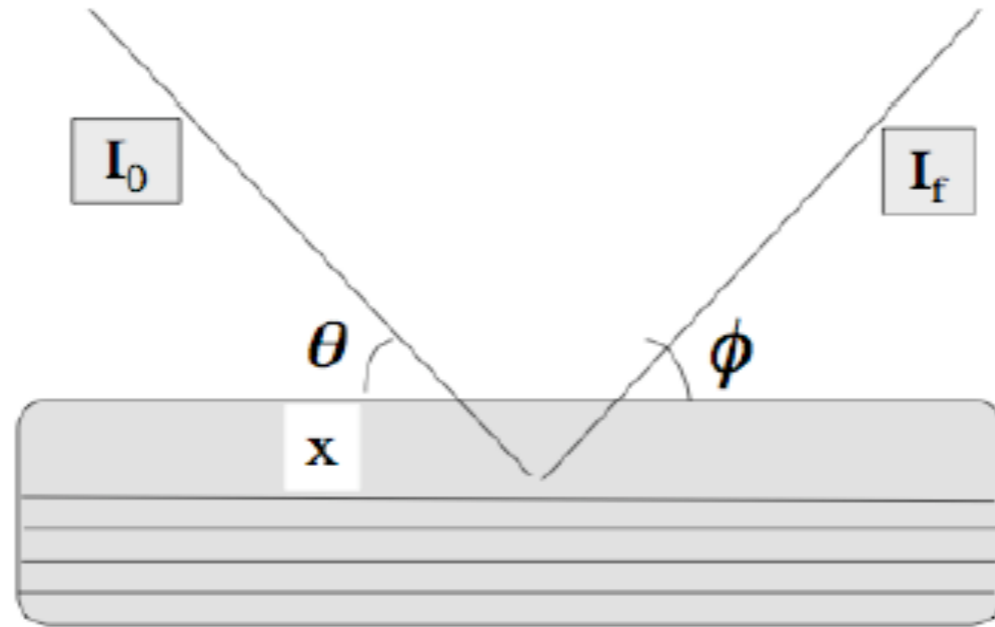
$$\eta \rightarrow 1$$

$$C_f \rightarrow 1$$

$$f(x) = \delta(x - a)$$
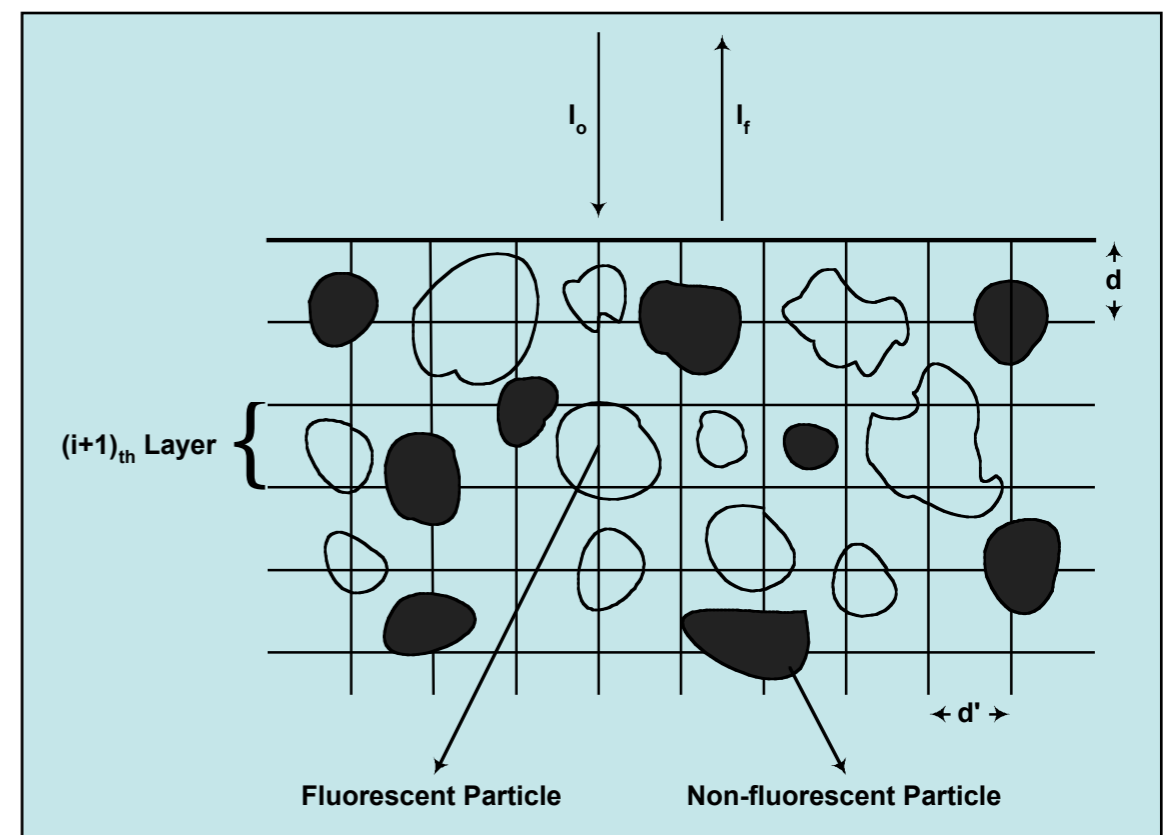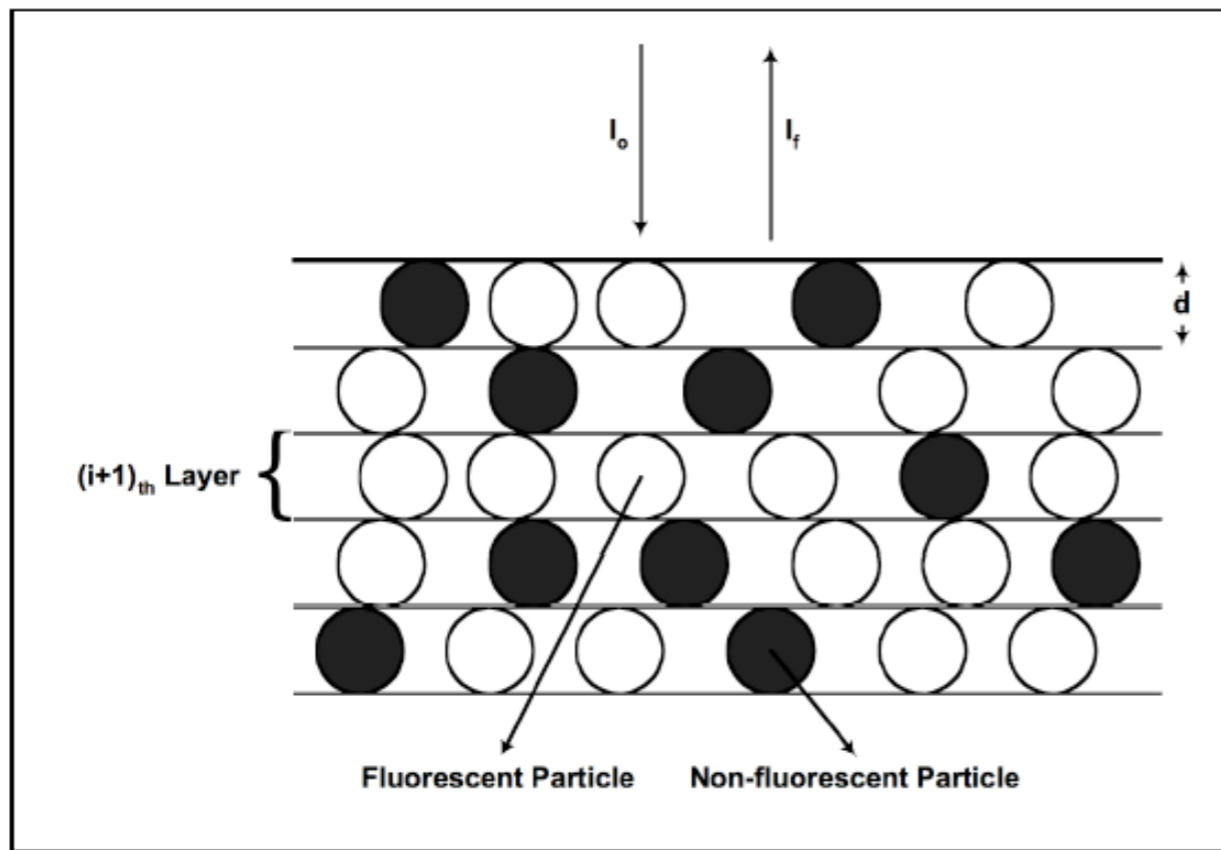
Comparison between BFR, HR, and Slab Model

Fluorescence in BFR Model and Slab Model
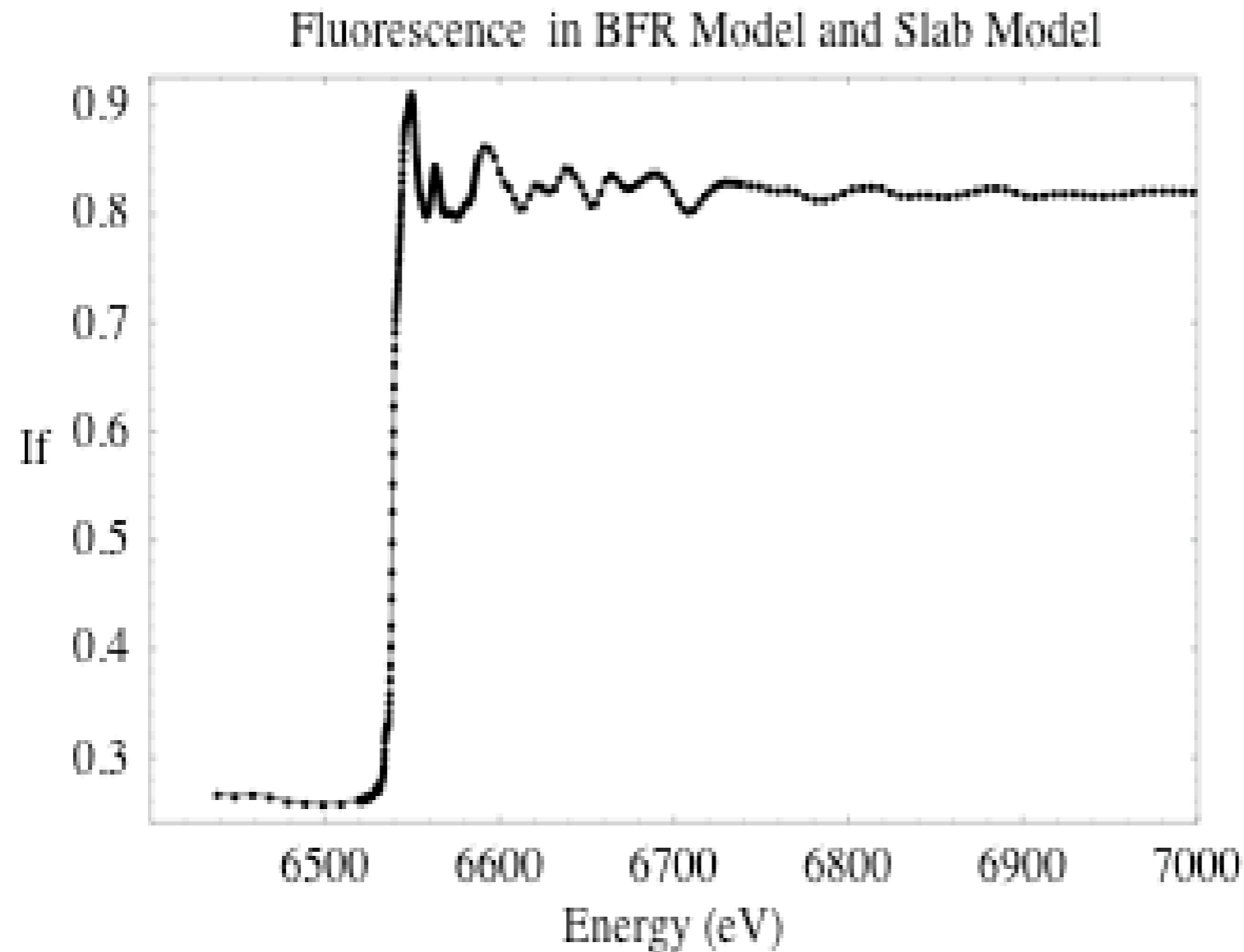
All 3 models agree in the appropriate limits

Summary - Fluorescence

- Particle size effects are important in fluorescence as well as transmission

- The homogeneous slab model is not always suitable but other models have been developed

- If the particles are not sufficiently small, their shape, orientation, and distribution can affect the spectra in ways that can influence results

- Particularly important for XANES and speciation fitting

Electron yield detection

- sample placed atop and electrically connected to cathode of helium filled ion chamber

- electrons ejected from surface of sample ionize helium - their number is proportional to absorption coefficient

- The current is collected as the signal just like an ionization chamber

- Surface sensitivity of electron detection eliminates self-absorption problems but does not probe the bulk material

Sample Inhomogeneities

- Importance of inhomogeneity also can depend on spatial structure in beam

    - bend magnets and wiggler beams usually fairly homogeneous

- Undulator beams trickier because beam partially coherent

    - coherence effects can result in spatial microstructure in beam at micron scales

- Beam Stability

- Samples must not have spatial structure on the same length scales as x-ray beam. Change the sample, or change the beam.

- Foils and films often make good transmission samples

    - stack multiple films if possible to minimize through holes

        - check for thickness effects (rotate sample)

- Foils and films can make good thin concentrated or thick dilute samples in fluorescence

- Consider grazing incidence fluorescence to reduce background and enhance surface sensitivity

Solutions

- Usually solutions are naturally homogeneous

    - Can make good transmission samples if concentrated

    - Usually make good fluorescence samples (~1 millimolar and 100 ppm are routine), lower concentrations feasible

    - They can become inhomogeneous during experiment

        - phase separation

        - radiation damage can cause precipitation (e.g. protein solutions)

        - photolysis of water makes holes in intense beams

        - suspensions/pastes can be inhomogeneous

Particulate samples

- First calculate the absorption length for the material

- prepare particles that are considerably smaller than one absorption length of their material, at an energy above the edge

- Many materials require micron scale particles for accurate results

- Distribute the particles uniformly over the sample cross sectional area by dilution or coating

Making Fine Particles

- During synthesis -> choose conditions to make small particles

- Grinding and separating

  - sample must not change during grinding (e.g. heating)

  - For XAFS can't use standard methods (e.g. heating in furnace and fluxing) from x-ray spectrometry, because chemical state matters

  - Have to prevent aggregation back into larger particles

Grinding Materials

- Dilute samples - have to prevent contamination

- mortar and pestle (porcelain or agate (a form of quartz))

- inexpensive small volume ball mill (e.g. "wig-l-bug" ~$700 US)

  - agate vials available

  - disposable plastic vials for mixing

  - standard for infrared spectrometry

- Frisch mill (several thousands of $K US)
  e.g. MiniMill 2 Panalytical, Gilson Micromill

Sieves

|	
100 mesh	150 μm
115 mesh	125 μm
150 mesh	106 μm
170 mesh	90 μm
200 mesh	75 μm
250 mesh	63 μm
270 mesh	53 μm
325 mesh	45 μm
400 mesh	38 μm
450 mesh	32 μm
500 mesh	25 μm
635 mesh	20 μm

- 3" ASTM sieves work well

  - Screen out larger particles with coarse mesh (100 mesh)

  - pass along to next finer sieve

  - Sieve stack and shaker

- Usually can do well with 100, 200, 325, 400, 500, 635 mesh

- Still only guarantees 20 micron particles, too big for many samples

size (microns) ~15000/mesh
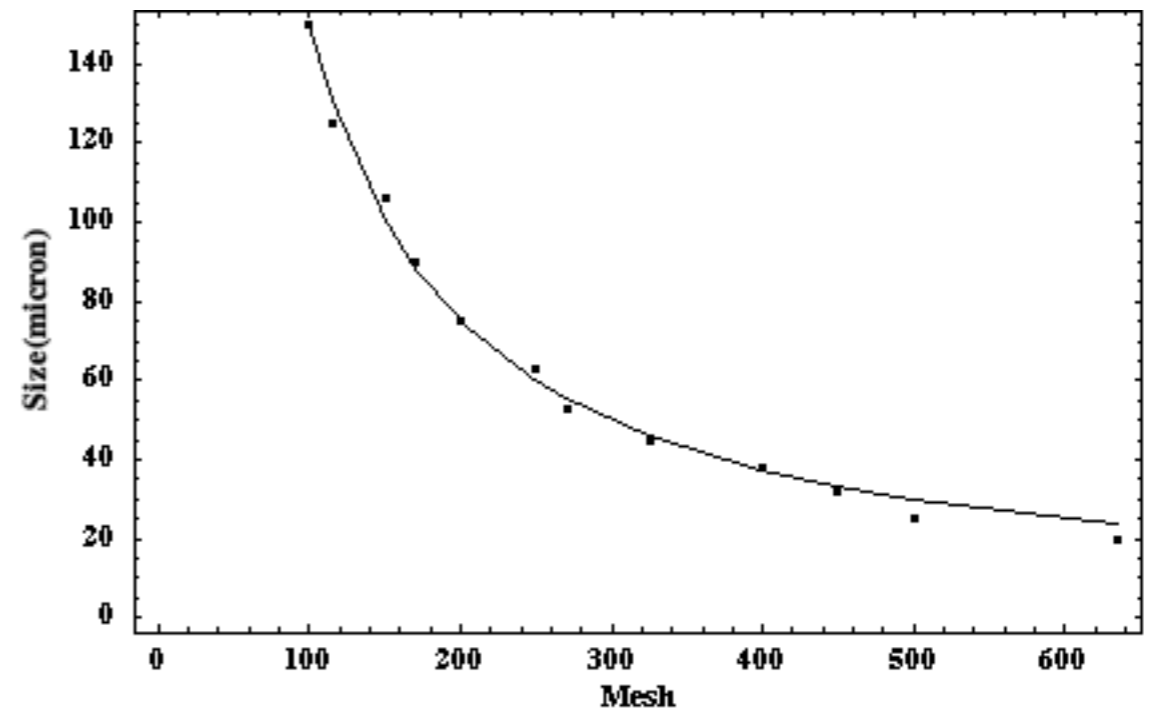
sedimentation

Selecting yet smaller particles

Drag force on a spherical particle of radius R moving at velocity v in fluid of viscosity η: $F = 6\pi\eta R v$. Particles of density ρ will fall through the fluid of density ρ_0 at a speed in which the particle's weight, less the buoyancy force, equals the drag force:

$$(\rho - \rho_0)\frac{4}{3}\pi R^3 g = 6\pi\eta R v.$$

If the height of the fluid in the container is h, the time t that it would take all particles of radius R to fall to the bottom would then be:

$$t = \frac{9}{5}\frac{\eta h}{(\rho - \rho_0)g R^2}$$

Sedimentation cont'd

- By knowing the densities of the material and the liquid (e.g. acetone), and the viscosity, the fluid height, and the required particle radius, you calculate the time.

- Mix it in, stir it up

  - wait the required time

  - decant the supernatant with a pipette

  - dry particles in a dish in a fume hood

- Must have non-reactive liquid

worked example

Example: MnO in acetone at 20C

viscosity of acetone :

$\eta = 0.0032$ Poise

$= 0.0032$ g/(cm $*$ s)

$R = 1\mu$m $= 3 * 10^{-4}$cm

density of acetone: $\rho_0 = 0.79\frac{g}{cm^3}$

density of MnO: $\rho = 5.4\frac{g}{cm^3}$

$h = 5$cm

$g = 980$cm/s^2

$\rightarrow t = 638$ seconds.

Assembling Samples

- A) Mix uniformly (use wig-l-bug) into filler or binder

  - nonreactive, devoid of the element you are measuring, made of a not-too-absorbant substance e.g. Boron Nitride, polyvinyl alcohol, corn starch

  - Place into a sample cell (x-ray transparent windows e.g kapton or polypropylene), or press to make pellet

- B) Apply uniform coating to adhesive tape

  - Scotch Magic Transparent Tape (clean, low absorption)

  - use multiple layers to cover gaps between particles

  - watch for brush marks/striations

- C) Make a "paint" (e.g. Duco cement thinned with acetone)

Checking the sample

- check composition by spectroscopy or diffraction

- visually check for homogeneity

  - caveat: x-ray vs optical absorption lengths

- tests at beamline: move and rotate sample

- digital microscope (Olympus Mic-D $800 US)

- particle size analysis (Image/J free)

- If you have nice instruments like a scanning electron microscope or light scattering particle size analyzer, don't hesitate to use them

Preferred Orientation

- If your sample is polycrystalline, it may orient in non-random way if applied to a substrate

- since the x-ray beams are polarized this can introduce an unexpected sample orientation dependence

- Test by changing sample orientation

- Magic-angle spinning to eliminate effect

Control samples

- In fluorescence measurements always measure a blank sample without the element of interest under the same conditions as your real sample

- Many materials have elements in them that you wouldn't expect that can introduce spurious signals

- Most aluminum alloys have transition metals

- Watch out for impurities in adhesive films

- Fluorescence from sample environment excited by scattered x-rays and higher energy fluorescence

HALO

- Harmonics

  - get rid of them

- Alignment

  - beam should only see uniform sample

- Linearity

  - detectors and electronics must linear

- Offsets

  - subtract dark currents regularly

Conclusion

- Absorption coefficients increase dramatically at low energies ~ $1/E^3$. Calculate the absorption coefficients so you know what you are dealing with at the energies you care about. Think like an x-ray. Know what to expect.

- Make particles much smaller than the absorption length above the edge, and ensure samples are homogeneous.
Check experimentally for thickness, particle size, and self absorption effects

- Make sure materials within the sample are not reactive with sample cell or windows.