BioCAT: Basic Techniques for EXAFS
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Thickness Effects in EXAFS spectra

Several experimental problems can cause insidious distortions of EXAFS amplitudes and XANES spectra. These errors usually can be avoided if care is taken in sample preparation, but they are all too easy to overlook, and are frequently ignored. Foremost among these problems are:

A) Thickness/particle size effects (sample nonuniformity and harmonics)
B) Self absorption effects in fluorescence

These experimental problems have been treated by several authors. For a more complete review of experimental difficulties, perusal of the review article by Heald[1] is highly recommended. The purposes of this technical note are to

Uniform sample

The attenuation of x-rays by a homogeneous amorphous or polycrystalline sample is usually well-represented by the equation $I=I_0 \exp(-\mu(E)x)$, where I_0 and I are respectively the x-ray flux incident on a sample and the flux transmitted through it. $\mu(E)$ is the absorption coefficient at x-ray energy E, and x is the sample thickness. The expression easily can be derived by assuming that a thin layer of sample of thickness δx decreases the beam intensity by a constant fraction $\mu\delta x$: $\delta I/I = -\mu\delta x$. Stacking up many thin layers to make a sample of finite thickness x gives the standard "Beer's law" equation above: $\int \delta I/I$ $=\ln(I)= -\int \mu\delta x = -\mu x+\text{const}$. This description presumes that the x-rays pass through the layers in series, that no part of the sample is bypassed. It also neglects interference effects such as diffraction and the Borrman effect.

The thickness μ^{-1} at which I/I_0 drops to 1/e is called one absorption length. If the sample consists of granules larger than one absorption length, interpretation of the spectra is more complicated. Similarly, if the sample consists of several types of particles of different composition, the absorption length must be long enough that many particles of each type are sampled by the x-ray beam, otherwise errors of interpretation may result.

Nonuniform sample

If the sample is nonuniform, the measured absorption $\mu(E)$ will differ from the true value. In this case, the sample area presented to the beam consists of regions of differing

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1 S.M. Heald, in "X-ray Absorption", Chapter 3, D.C. Koningsberger and R. Prins, eds., Wiley (1988)

thicknesses. Defining P(x) as the fraction of the sample area that is of thickness x, where $\int P(x)\,dx = 1$, the apparent absorption coefficient is just $\exp(-(\mu x)_{eff}) = \int P(x)\exp(-\mu x)\,dx$. The greater the variation in sample thickness, and the larger μ gets, the more the apparent absorption is suppressed. Such distortions are called "thickness effects".

For example, consider the case where a fraction f of the sample area has pinholes in it, and the rest is of uniform thickness x_0, so that a fraction of the beam "leaks through" the sample. Then $P(x) = f\,\delta(x) + (1-f)\,\delta(x-x_0)$ and $(\mu x)_{eff} = -\ln(f+(1-f)\exp(-\mu x_0))$. The apparent absorption $(\mu x)_{eff}$ is plotted vs the true absorption μx in figure 1 for several levels of leakage f. $(\mu x)_{eff}$ saturates at a value of ln(1/f) for large μ.

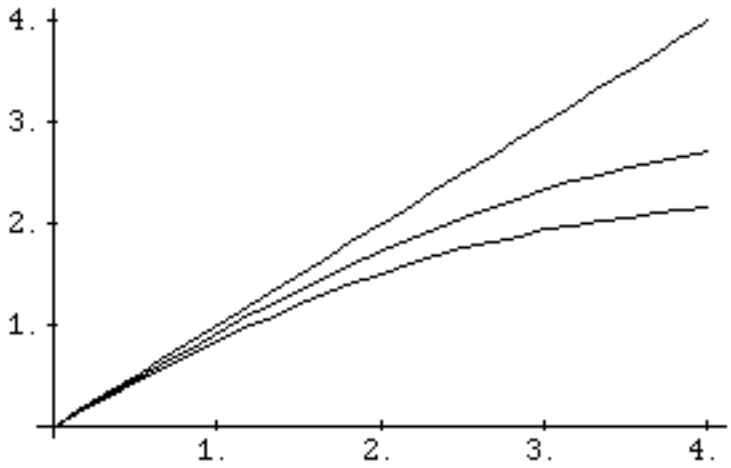

Figure 1: The apparent absorption $(\mu x)_{eff}$ is plotted vs the true absorption μx for 0%, 5%, and 10% leakage.

Another simple limiting case is that of a gaussian distribution in thickness:

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left(-\frac{(x-x_0)^2}{2\sigma^2}\right).$$

All cumulants of order higher than the second are zero for a gaussian, so the series only has two terms: $(\mu x)_{eff} = \mu x_0 - \frac{1}{2}\mu^2\sigma^2$. Note that this form breaks down for large μ, because the gaussian has a small but finite tail at negative thickness, which becomes troublesome as $\mu\sigma$ gets large.

In general the apparent absorption coefficient can be expanded as:

$$(\mu x)_{eff} = -\sum_{n=0} \frac{(-\mu)^n C_n}{n!},$$

where the coefficients C_n are called the "cumulants" of P(x). The first cumulant of P(x), C_1, is just the average thickness <x>; the second, C_2, is the mean square variation in

thickness: $\langle (x-\langle x\rangle)^2\rangle$. $C_3=\langle (x-\langle x\rangle)^3\rangle$ depends on the amount the distribution P(x) is skewed. Because C_2 is always positive, the initial curvature of a plot of $(\mu x)_{eff}$ vs μ is always negative. In fact, the curvature of the function

$$(\mu x)_{eff} = f(\mu) = -\ln \left[\int P(x)\, \exp(-\mu x)\, dx \right]$$

is negative (or zero) for all values of x, as can be readily shown by differentiating twice with respect to μ. In fact, you can verify for yourself that the slope and curvature at *any* value of μ are just the first and second cumulant (mean position and mean squared width) of the modified distribution $Q(x;\mu)=P(x)\exp(-\mu x)$. Both of these are non-negative, and tend to zero for large μ for any continuous P(x) (as long as P(x)=0 for x<0, i.e. negative thicknesses aren't allowed). In summary, a plot of $(\mu x)_{eff}$ vs μ tends to a straight line for large μ. The slope of this line is the effective thickness of the sample. Evidently, if the absorption coefficient is large enough, the slope corresponds to the true thickness of the thinnest part of the sample. If the sample has pinholes, the $(\mu x)_{eff}$ vs μ curve asymptotes to a constant value (slope zero) of ln(1/f), where f is the fraction of the sample area with pinholes.

Ok, fine, but what does this have to do with EXAFS? The crucial point is that thickness effects always *suppress* EXAFS amplitudes, even when one normalizes the data by dividing by the measured edge step. Normalizing the wiggles in this manner does tend to compensate somewhat for the spurious amplitude reduction, but it doesn't do the whole job. The following derivation, together with the previous discussion, treats the general case.

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

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

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 $\chi = \dfrac{(\mu_a+\delta\mu)-(\mu_a)}{\mu_a-\mu_b} = \dfrac{\delta\mu}{\mu_a-\mu_b}$. Thus, thickness effects alter the measured EXAFS amplitudes by the ratio: $\dfrac{\chi_{eff}}{\chi} = \dfrac{df}{d\mu}\Big|_{\mu a} \dfrac{\mu_a-\mu_b}{f(\mu_a)-f(\mu_b)}$. To evaluate the right side of this equation, consider the taylor expansion:

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

This can be rewritten:

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

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.