

Let $S = \{s_1, \dots, s_n\}$ be a set of n standards, with concentrations $X = \{x_1, \dots, x_n\}$ and measurements $Y = \{y_1, \dots, y_n\}$.

The Four parameter logistic curve we will try to fit is defined as

$$f(x) = d + \frac{a - d}{1 + \left(\frac{x}{c}\right)^b}.$$

Each of the parameters serve a purpose:

- a is the lower asymptotic bound of f
- d is the upper asymptotic bound of f
- c determines the point of inflection of the curve
- b determines the slope at the point of inflection

We will try to find a local minimum for a, b, c and d using gradient descent.

When plotted on a graph with a logarithmic scaling x-axis, it has a sigmoidal shape, so we will substitute x with $\hat{x} = \ln x \Leftrightarrow x = e^{\hat{x}}$. Moreover we want c to scale proportionally with the point of inflection, so we will substitute it with $\hat{c} = \ln c \Leftrightarrow c = e^{\hat{c}}$. This gives us

$$f(x) = d + \frac{a - d}{1 + \left(\frac{e^{\hat{x}}}{e^{\hat{c}}}\right)^b} = d + \frac{a - d}{1 + e^{b(\hat{x} - \hat{c})}}$$

Our cost function shall be the sum of squares.

$$C(Y, X, a, b, c, d) = \frac{1}{n} \sum_{i=1}^n (y_i - f(x_i))^2$$

First we compute mutual parts of the derivatives

$$\begin{aligned} C(v) &= \frac{1}{n} \sum_{i=1}^n v^2, \quad v(y, u) = y - u, \quad u(\hat{x}, a, b, \hat{c}, d) = d + \frac{a - d}{1 + e^{b(\hat{x} - \hat{c})}} \\ \frac{\partial C(v)}{\partial v} &= \frac{\partial}{\partial v} \frac{1}{n} \sum_{i=1}^n v^2 = \frac{1}{n} \sum_{i=1}^n \frac{\partial}{\partial v} v^2 = \frac{1}{n} \sum_{i=1}^n 2v = \frac{2}{n} \sum_{i=1}^n v \\ \frac{\partial v}{\partial u} &= \frac{\partial}{\partial u} (y - u) = -1 \end{aligned}$$

We take the partial derivative of u with respect to a, b, \hat{c} and d .

$$\begin{aligned} \frac{\partial u}{\partial a} &= \frac{1}{1 + e^{b(\hat{x} - \hat{c})}} \\ \frac{\partial u}{\partial b} &= -\frac{(a - d)(\hat{x} - \hat{c})e^{b(\hat{x} - \hat{c})}}{(1 + e^{b(\hat{x} - \hat{c})})^2} \\ \frac{\partial u}{\partial \hat{c}} &= \frac{b(a - d)e^{b(\hat{x} - \hat{c})}}{(1 + e^{b(\hat{x} - \hat{c})})^2} \\ \frac{\partial u}{\partial d} &= \frac{1}{1 + e^{b(\hat{x} - \hat{c})}} \end{aligned}$$

Now, putting it all together

$$\begin{aligned}
\frac{\partial C(v)}{\partial a} &= \frac{\partial C(v)}{\partial u} \frac{\partial u}{\partial a} = -\frac{2}{n} \sum_{i=1}^n \left(y_i - d - \frac{a-d}{1+e^{b(\hat{x}_i-\hat{c})}} \right) \frac{1}{1+e^{b(\hat{x}_i-\hat{c})}} \\
\frac{\partial C(v)}{\partial b} &= \frac{\partial C(v)}{\partial u} \frac{\partial u}{\partial b} = -\frac{2}{n} \sum_{i=1}^n \left(y_i - d - \frac{a-d}{1+e^{b(\hat{x}_i-\hat{c})}} \right) \cdot \left(-\frac{(a-d)(\hat{x}_i-\hat{c})e^{b(\hat{x}_i-\hat{c})}}{(1+e^{b(\hat{x}_i-\hat{c})})^2} \right) \\
&= \frac{2}{n} (a-d) \sum_{i=1}^n \left(y_i - d - \frac{a-d}{1+e^{b(\hat{x}_i-\hat{c})}} \right) \frac{(\hat{x}_i-\hat{c})e^{b(\hat{x}_i-\hat{c})}}{(1+e^{b(\hat{x}_i-\hat{c})})^2} \\
\frac{\partial C(v)}{\partial \hat{c}} &= \frac{\partial C(v)}{\partial u} \frac{\partial u}{\partial \hat{c}} = -\frac{2}{n} \sum_{i=1}^n \left(y_i - d - \frac{a-d}{1+e^{b(\hat{x}_i-\hat{c})}} \right) \frac{b(a-d)e^{b(\hat{x}_i-\hat{c})}}{(1+e^{b(\hat{x}_i-\hat{c})})^2} \\
&= -\frac{2}{n} b(a-d) \sum_{i=1}^n \left(y_i - d - \frac{a-d}{1+e^{b(\hat{x}_i-\hat{c})}} \right) \frac{e^{b(\hat{x}_i-\hat{c})}}{(1+e^{b(\hat{x}_i-\hat{c})})^2} \\
\frac{\partial C(v)}{\partial d} &= \frac{\partial C(v)}{\partial u} \frac{\partial u}{\partial d} = -\frac{2}{n} \sum_{i=1}^n \left(y_i - d - \frac{a-d}{1+e^{b(\hat{x}_i-\hat{c})}} \right) \frac{1}{1+e^{b(\hat{x}_i-\hat{c})}}.
\end{aligned}$$

Note that

$$\begin{aligned}
&\sum_{i=1}^n \left(y_i - d - \frac{a-d}{1+e^{b(\hat{x}_i-\hat{c})}} \right) \cdot g(x_i) \\
&= \sum_{i=1}^n y_i \cdot g(x_i) - d \sum_{i=1}^n g(x_i) - (a-d) \sum_{i=1}^n \frac{g(x_i)}{1+e^{b(\hat{x}_i-\hat{c})}}
\end{aligned}$$

so the function can be split up further, reducing total operations per iteration