Two of the most ubiquitous computational methodologies in use are solving ordinary differential equation systems and estimating parameters via curve-fitting. An area where these two methodologies converge is the domain of chemical kinetics.

Below we show an interesting example of such modeling for dimer kinetics. Suppose we have two substances, \( A \) and \( B \) which bind to form a complex \( C \), and the substance \( C \), in turn, binds with itself to form a dimer \( D \). We thus have:

\[
A + B \xrightarrow{k_1} C, \quad C \xrightarrow{k_3} D.
\]

Suppose further we mix 2 mmoles of \( A \) and 3 mmoles of \( B \) and measure the concentration in mmoles of both \( C \) and \( D \) at ten equally-spaced times between 0 and 70 seconds. From this data we wish to estimate the association and dissociation constants \( k_1, k_2, k_3, \) and \( k_4 \).

The MLAB advanced mathematical and statistical modeling system is a convenient tool for mathematical modeling; in particular, it is designed to handle the curve-fitting of differential equation models to data. We may proceed in MLAB as follows.

First we read in the data consisting of values of \( c(t) \) and \( d(t) \) given at the common times 0 : 70l10. Although common times are used here, this is not required.

```mlab
* data = (0:70!10) &' read(ddata,10,2)
* type data
    time  c   d
 1: 0   0   0
 2: 7.778  0.6702  0.0426
 3: 15.56  1.039  0.1481
```
Now we define our kinetic model so that \(c(t)\) is the concentration of \(c\) in mmoles at time \(t\) and \(d(t)\) is the concentration of \(d\) in mmoles at time \(t\).

\[
\begin{align*}
\text{fct } c'(t) &= k_1 ((a_0 - c - 2*d)*(b_0 - c - 2*d)) - k_2 * c - 2*d' \cdot (t) \\
\text{fct } d'(t) &= k_3 * c * c - k_4 * d \\
\text{initial } c(0) &= 0 \\
\text{initial } d(0) &= 0 \\
\text{a0} &= 2; \text{b0} = 3
\end{align*}
\]

Now we guess the values of \(k_1, k_2, k_3,\) and \(k_4\). We may use the results of equilibrium studies, analyzed by MLAB, to know values for the ratios \(k_1/k_2\) and \(k_3/k_4\).

\[
\begin{align*}
k_1 &= 0.02; k_2 = 0.002; k_3 = 0.02; k_4 = 0.002 \\
\text{constraints } q &= \{k_1 > 0, k_2 > 0, k_3 > 0, k_4 > 0\}
\end{align*}
\]

Now we may curve-fit the two ode-system-defined functions, \(c\) and \(d\), to estimate \(k_1, k_2, k_3,\) and \(k_4\).

\[
\begin{align*}
\text{fit}(k_1, k_2, k_3, k_4), \text{ c to cdata, d to ddata, constraints } q \text{final parameter values}
\end{align*}
\]

<table>
<thead>
<tr>
<th>value</th>
<th>error</th>
<th>dependency parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06916895493</td>
<td>0.02023902877</td>
<td>0.5830898606</td>
</tr>
<tr>
<td>0.01003638127</td>
<td>0.01500173275</td>
<td>0.5933235047</td>
</tr>
<tr>
<td>0.01427015399</td>
<td>0.002713671566</td>
<td>0.7642104538</td>
</tr>
<tr>
<td>3.458442141e-20</td>
<td>0.00396602698</td>
<td>0.7396366489</td>
</tr>
</tbody>
</table>

4 iterations
CONVERGED

best weighted sum of squares = 2.184931e-01
weighted root mean square error = 1.168581e-01
weighted deviation fraction = 1.207618e-01

Now we may draw the results of the curve-fit.

* m=integrate(c't,d't,0:100!140)
* draw m col (1,2) color red
* draw m col (1,4) color green lt dashed
* draw cdata pt circle lt none color red
* draw ddata pt circle lt none color green
* bottom title "time in seconds"
* left title "mmoles (C and D)"

* oformat = nformat; nformat ="%4.4lf"
* v=strval(stdest[1]); s=strval(k1)+'25TF'R +substr(v,strlen(v))
* title s at (.6,.8) ffract size .015
* v=strval(stdest[2]); s=strval(k2)+'25TF'R +substr(v,strlen(v))
* title s at (.6,.75) ffract size .015
* v=strval(stdest[3]); s=strval(k3)+'25TF'R +substr(v,strlen(v))
* title s at (.6,.7) ffract size .015
* v=strval(stdest[4]); s=strval(k4)+'25TF'R +substr(v,strlen(v))
* title s at (.6,.65) ffract size .015
* nformat=oformat

* view
Fit of Kinetic Data for Dimer ODE Model

- $K_1 = 0.0683 \pm 0.0155$
- $K_2 = 0.0092 \pm 0.0131$
- $K_3 = 0.0143 \pm 0.0028$
- $K_4 = 0 \pm 0.0042$

MLAB is a product of Civilized Software, Inc. The URL is http://www.civilized.com.