Theory

Suppose there are n monomers species. Let

$$M = (M_1, M_2, \ldots, M_n) \in \mathbb{R}^d$$

denote the vector of monomer concentrations, and

$$M^* = (M_1^*, M_2^*, \ldots, M_n^*) \in \mathbb{R}^d$$

denote the vector of concentrations of chains terminating in monomer $(M_1, M_2, \ldots, M_n)$ respectively. Let us also write the rate constant matrix as

$$K \in \mathbb{R}^{n \times n}$$

We shall assume that K is in general position, i.e. K is invertible and diagonalizable (which happens almost surely if this is measured with some random error)

Then, the generalized n-monomer Mayo-Lewis reaction is given by

$$M_i^* + M_j \xrightarrow{K_{ij}} M_j^*, \qquad i, j = 1, 2, \ldots, n$$

The rate equations are the following system of ODEs (written in vector form)

$$\begin{aligned} \frac{dM}{dt} &= -(K^T M^*) \circ M \\ \frac{dM^*}{dt} &= (K^T M^*) \circ M - (KM) \circ M^* \end{aligned}$$

where K^T is the transpose of the matrix K amd $\circ$ denotes vector Hadamard product, i.e. for vectors x and y, $x \circ y$ is a vector with components $x \circ y = (x_1 y_1, x_2 y_2, \ldots, x_n y_n)$.

Now, let us denote by $\mathbf{1}$ the vector of all 1's, i.e. $\mathbf{1} = (1, 1, \ldots, 1)$. Then, the monomer mole fraction is a vector

$$f = \frac{M}{\mathbf{1}^T M}$$

Similarly, the fraction of chains terminating in monomers f is

$$f^* = \frac{M^*}{\mathbf{1}^T M^*}$$

Finally, under the steady-state condition the mole fraction of incorporated moonomer is a vector

$$F = \frac{dM/dt}{\mathbf{1}^T dM/dt}$$

We shall assume that M, M^* and dM/dt are not identically 0 so that the above expressions for f, f^*, F are well-defined.

Using the steady-state approximation, we may set $dM^*/dt = 0$. This allows us to write, using the ODE system, the following equations

$$F = \frac{f \circ K^T f^*}{f^T K^T f^*}$$
$$0 = (K^T f^*) \circ f - (Kf) \circ f^*$$

The last equation can be rewritten

$$(D_f K^T - D_{Kf}) f^* = 0$$

where for any vector x, D_x denotes the diagonal matrix formed by having x on the diagonal and 0 everywhere else. Since K is in general position, the matrix $A(K, f) \equiv (D_f K^T - D_{Kf})$ has a one-dimensional null-space, whose basis we denote by the vector $v_0(K, f)$. Then, we immediately have

$$f^* = \frac{v_0(K, f)}{\mathbf{1}^T v_0(K, f)}$$

Therefore, we have the relationship between F and f

$$F = \frac{f \circ K^T v_0(K, f)}{f^T K^T v_0(K, f)}$$

Conversely, given F we can also determine f, but this is in general no longer a one-to-one mapping, hence we may resort to solving the optimization problem

$$f = \underset{x: x_i \geq 0, \sum_i x_i = 1}{\arg\min} \left\| F - \frac{x \circ K^T v_0(K, x)}{x^T K^T v_0(K, x)} \right\|^2$$

which can be solved numerically by the L-BFGS-B method.