Singular perturbation treatment of the decomposition of ozone
3. Geometric singular perturbation theory

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October 29, 2019

In the previous two lectures, we determined the conditions for the validity of the steady-state approximation in an ozone decomposition mechanism, and then assuming that these conditions held, we worked out an approximate solution to the differential equations. What if the steady-state approximation is actually a poor approximation? Can we improve on it? One approach to doing this is geometric singular perturbation theory. Note that the steady-state approximation gives us a differentiable (but not invariant) manifold relating the phase-space coordinates, of the form

$$y = y_{\mathcal{S}}(x).$$

One way to understand Tikhonov's theorem is that it tells us that $y_{\mathcal{S}}(x)$ is close to an invariant manifold that trajectories follow down to the equilibrium point after the decay of transients. This manifold is called a **slow manifold**, $\mathcal{M}$. $\mathcal{M}$ is an invariant manifold that comes into the equilibrium point along the slow eigenvector. But we know that invariant manifolds must satisfy the invariance equation:

$$\frac{dy}{d\tau} = \frac{dy_{\mathcal{M}}}{dx}\frac{dx}{d\tau}.$$

So how do we solve the invariance equation? There are many methods, but in the spirit of singular perturbation theory, we're going to expand $y_{\mathcal{M}}(x)$ in a series in the parameter ϵ. This approach is known as **geometric singular perturbation theory**.

Our rate equations are

$$\frac{dx}{d\tau} = -x + \alpha y - (1-\alpha)xy,$$
$$\epsilon\frac{dy}{d\tau} = x - \alpha y - (1-\alpha)xy.$$

We want to write $y_{\mathcal{M}}$ in the form

$$y_{\mathcal{M}}(x) = \phi_0(x) + \epsilon\phi_1(x) + \epsilon^2\phi_2(x) + O(\epsilon^3),$$

where the functions $\phi_i(x)$ are unknown functions. We substitute our ansatz for $y_{\mathcal{M}}$ into the invariance equation:

$$\begin{aligned}
&\frac{1}{\epsilon}\left\{x - \left[\phi_0(x) + \epsilon\phi_1(x) + \epsilon^2\phi_2(x) + O(\epsilon^3)\right][\alpha + (1-\alpha)x]\right\} \\
&\quad = \left[\frac{d\phi_0}{dx} + \epsilon\frac{d\phi_1}{dx} + \epsilon^2\frac{d\phi_2}{dx} + O(\epsilon^3)\right] \\
&\qquad\qquad \times \left\{-x + \left[\phi_0(x) + \epsilon\phi_1(x) + \epsilon^2\phi_2(x) + O(\epsilon^3)\right][\alpha - (1-\alpha)x]\right\}
\end{aligned}$$

$$\begin{aligned}
&\therefore x - \left[\phi_0(x) + \epsilon\phi_1(x) + \epsilon^2\phi_2(x) + O(\epsilon^3)\right][\alpha + (1-\alpha)x] \\
&\quad = \epsilon\left[\frac{d\phi_0}{dx} + \epsilon\frac{d\phi_1}{dx} + \epsilon^2\frac{d\phi_2}{dx} + O(\epsilon^3)\right] \\
&\qquad\qquad \times \left\{-x + \left[\phi_0(x) + \epsilon\phi_1(x) + \epsilon^2\phi_2(x) + O(\epsilon^3)\right][\alpha - (1-\alpha)x]\right\}
\end{aligned}$$

All we have to do now is to collect terms in different powers of ϵ across both sides of the equation, and solve for each of the $\phi_i(x)$.

ϵ^0:

$$x - \phi_0(x)[\alpha + (1-\alpha)x] = 0.$$
$$\therefore \phi_0(x) = \frac{x}{\alpha + (1-\alpha)x}.$$

> You may recognize this as the steady-state approximation. The zero-order term in geometric singular perturbation theory will typically be the steady-state approximation.

ϵ^1**:**

$$-\phi_1(x)\left[\alpha+(1-\alpha)x\right]=\frac{d\phi_0}{dx}\left\{-x+\phi_0(x)\left[\alpha-(1-\alpha)x\right]\right\}$$
$$\frac{d\phi_0}{dx}=\frac{\alpha}{\left[\alpha+(1-\alpha)x\right]^2}$$

$$\therefore \phi_1(x)=\frac{\alpha}{\left[\alpha+(1-\alpha)x\right]^2}\frac{x-\frac{x}{\alpha+(1-\alpha)x}\left[\alpha-(1-\alpha)x\right]}{\alpha+(1-\alpha)x}$$
$$=\frac{2\alpha x^2(1-\alpha)}{\left[\alpha+(1-\alpha)x\right]^4}$$

ϵ^2**:**

$$-\phi_2(x)\left[\alpha+(1-\alpha)x\right]$$
$$=\frac{d\phi_0}{dx}\phi_1(x)\left[\alpha-(1-\alpha)x\right]+\frac{d\phi_1}{dx}\left\{-x+\phi_0(x)\left[\alpha-(1-\alpha)x\right]\right\}$$

It would not be difficult to get an explicit expression for $\phi_2(x)$, but you can see that this is getting tedious. It might make sense to use Maple…