Using Homotopy Continuation to Solve Chemical Equilibrium Problems

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1 Homotopy Continuation

1.1 Total Degree Homotopy Continuation

We wish to solve for $F(x_1, ..., x_n)$ by numerically solving (1) through tracking a known starting system $H_0 = S(x_1, ..., x_n)$ as it deforms to H_1 with the continuation parameter $t \in [0, 1]$.

$$H(x_1, x_2..., x_n, t) = (1 - t)S_{starting} + tF \tag{1}$$

The starting system $S(x_1, ..., x_n)$ is based on the solutions of the highest degree monomial in $F(x_1, ..., x_n)$ as such:

$$S(x_1, ..., x_n) = \begin{pmatrix} X_1^n - 1 \\ X_2^n - 1 \\ ... \\ X_n^n - 1 \end{pmatrix} \tag{2}$$

The value of
To be able to solve for solutions at infinity, we must convert these complex cartesian coordinates to a complex homogeneous coordinate system. This is done by introducing a new homogenizing variable z_0 as such:

$$P(z_0 z_1, z_2, ...z_n) = z_0^{d_n} F(\frac{x_1}{z_0}, \frac{x_2}{z_0}, ..., \frac{x_n}{z_0}) \tag{3}$$

However, we must apply a projective transformation using an euclidean patch to essentially track only the cross section of the projective space using a random complex coefficients α_n as such:

$$\alpha_1 x_1 + \alpha_2 x_2 + ... + \alpha_n x_n = 1 \tag{4}$$

A predictor-corrector scheme is utilized to numerically track the homotopy H. An adaptive time step algorithm is also implemented to increase the efficiency and accuracy of the tracker. After ≤ 3 corrector attempts is made and the residual is still above a heuristically defined correction criterion, the timestep dt will be halved. Similarly, if three successful tracking steps were executed, dt will be doubled. The predictor involves solving the Davidenko differential equation:

$$p(z_0, z_1, ..., z_n) = \boldsymbol{J_f}^{-1} \frac{\partial H}{\partial t} \tag{5}$$

Newton's predictor will then be subsequently implemented to 'correct' the estimation:

$$c(z_0, z_1, ..., z_n) = (\frac{\partial H}{\partial t})^{-1} H \tag{6}$$

As $t \to 1$, singular solutions may become ill conditioned and must be removed in order to advance. Two approaches were taken at the heuristically determined 'endzone region' to truncate any ill-conditioned tracked solutions. The first endgame is to calculate the norm of the condition number of $\boldsymbol{J_f}$ and compare it to a predefined threshold. But as $t \approx 1$, we calculate the residual of $H(x_1, x_2..., x_n, t)$ and compare it to $H(x_1, x_2..., x_n, 1.0)$.

1.2 Parameter Homotopy

For a generic class of polynomial with linear coefficients, a homotopy can be constructed between the same system of polynomial with different coefficients. A random set of complex coefficients is used first in a total degree homotopy to calculate the tracking solutions for the parameter homotopy.

2 Saturated Silver Chloride in solution

The continuation method outlined in section 1 is applied to solve a chemical equilibrium problem. The chemical reactions is outlined here:

$$AgCl^2_{(s)} \leftrightarrow Ag^+ + Cl^-$$
$$Ag^+ + OH^- \leftrightarrow AgOH$$
$$Ag^+ + Cl^- \leftrightarrow AgCl$$
$$AgCl + Cl^- \leftrightarrow AgCl_2^-$$
$$AgCl + Ag^+ \leftrightarrow Ag_2Cl^+$$
$$AgCl_2^+ + Cl^- \leftrightarrow AgCl_3^{--}$$
$$AgCl_2^+ + Ag^+ \leftrightarrow Ag_3Cl^{++}$$
$$H_2O_{(l)} \leftrightarrow H_+ + OH^-$$

Saturation States:

$$[AgCl_{(s)}] = 1$$
$$[H_2O_{(l)}] = 1$$

Total Conservation of Species:

$$Ag^+ + AgOH + AgCl + AgCl_2^- + 2Ag_2Cl^+ + AgCl_3^{--} + 3Ag_3Cl^{++} = S_{Ag}$$
$$Cl^- + AgCl + 2AgCl_2^- + Ag_2Cl^+ 3AgCl_3^{--} + Ag_3Cl^{++} = S_{Cl}$$
$$OH^- + AgOH = S_{OH}$$
$$H^+ = S_H$$

Equilibrium Constants:

$$K_1 = \frac{[Ag^+][Cl^-]}{[AgCl_{(s)}]}$$
$$K_2 = \frac{[AgOH]}{[Ag^+][OH^-]}$$
$$K_3 = \frac{[AgCl]}{[Ag^+][Cl^-]}$$
$$K_4 = \frac{[AgCl_2^-]}{[AgCl][Cl^-]}$$
$$K_5 = \frac{[Ag_2Cl^-]}{[AgCl][Ag]}$$
$$K_6 = \frac{[AgCl_3^{--}]}{[AgCl_2^-][Cl^-]}$$
$$K_7 = \frac{[Ag_3Cl^{++}]}{[Ag^+][AgCl_3^{--}]}$$
$$K_8 = \frac{[H^+][OH-]}{[H_2O_{(l)}]}$$

Using a heuristic method of reduction introduced by Keith Meintjes this is the resulting polynomial system:

$$\alpha_1[Ag^+]^4 + \alpha_2[Ag^+]^3[Cl^-] + \alpha_3[Ag^+]^3 + \alpha_4(Ag^+) + \alpha_5 = 0 \tag{7}$$

$$\beta_1[Ag^+][Cl^-]^2 + \beta_2[Cl^-]^2 + \beta_3 = 0 \tag{8}$$

Resulting polynomial coefficients:

$$\alpha_1 = 2K_1K_3K_5K_7$$
$$\alpha_2 = K_2$$
$$\alpha_3 = K_1K_3K_5 + 1$$
$$\alpha_4 = -K_1(K_1K_3K_4 + 1)$$
$$\alpha_5 = -2K_1^3K_3K_4K_6$$
$$\beta = \frac{K_2}{K_8}$$
$$\beta = \frac{1}{K_8}$$
$$\beta = -1$$

3 Results

9 non-singular solutions were tracked from a starting solution of 12 using a total degree homotopy continuation with random complex coefficients.

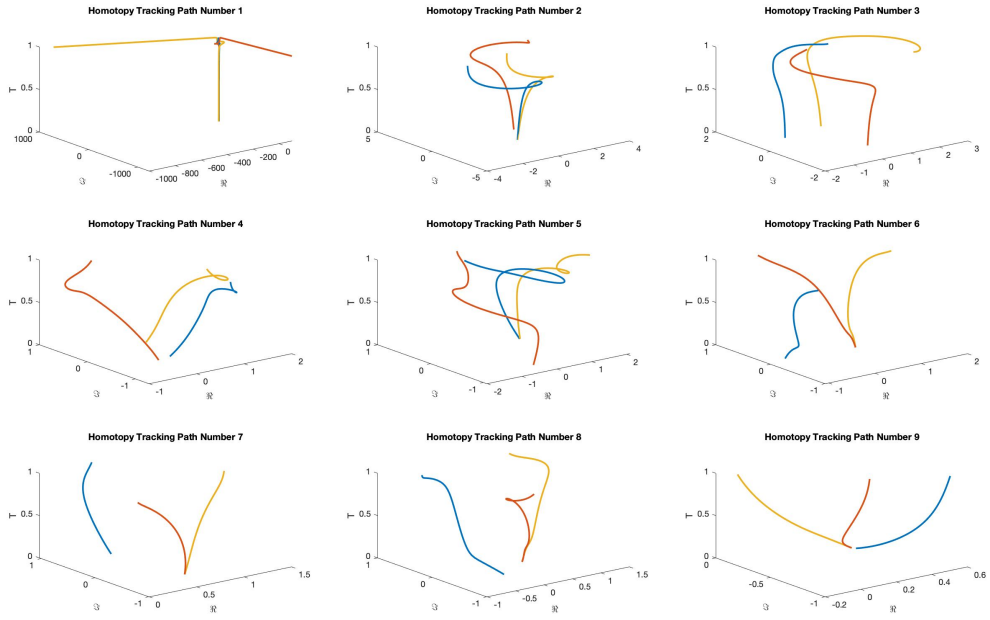

Figure 1: Tracked paths of the 9 non-singular complex solutions.