Methodology for a nullcline-based model from direct experiments: Applications to electrochemical reaction models

Michael J. Hankins, Timea Nagy, István Z. Kiss

Department of Chemistry, Saint Louis University, 3501 Laclede Ave, St Louis, 63123, United States

ARTICLE INFO

Keywords:
Manifold
Oscillation
Bistability
Excitability
Model simplification

ABSTRACT

A method is proposed for the construction of simple yet accurate mathematical models for description of dynamics of nonlinear systems based on the concept of nullclines. The nullclines are functional relationships between the essential variables of a dynamical system where the rate of change of a species is constrained to zero. When the time scales of the essential variables are separated the dynamics can often be described by motion along nullclines of the fast variable. We propose a methodology with which the nullclines can be obtained from direct control experiments. The goal is achieved by a combination of an adaptive and proportional controller acting on the fast and the slow variables of the system. It is demonstrated in the numerical simulations of two- and three-variable electrochemical models that the nullclines can be extracted from control of experimentally feasible control parameters (circuit potential and rotation rate). As an extension of the methodology, we propose a nullcline based technique which is capable of reproducing the temporal behavior of the system’s variables (e.g., waveform of the oscillations). The numerical simulations indicate that the nullcline based model information from direct experiments can effectively predict the system’s dynamics and thus the technique holds promise for an alternative modeling route to traditional kinetics/mass transfer based approaches.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Complex dynamical features of multicomponent chemical reacting systems such as oscillations, multistability, and excitability often can be explained with low dimensional (two and three variable) models [1,2]. The development of such simplified yet accurate models is a challenging task; the mathematical approaches [3] greatly depend on the type of desired dynamical features that need to be reproduced (e.g., number of stability of steady states, types of synchronization, relaxation timescales). Because many dynamical features are associated with bifurcations at critical values of system parameters, bifurcation theory has been very successful for the development of low-dimensional mathematical models: when an experiment exhibited a certain type of bifurcation, the mathematical structure for that particular type of bifurcation is expected to arise and thus can be used as an initial guideline for model development. With methodologies that rely on control of important system parameters [4–8], bifurcation diagrams can be experimentally reconstructed and the bifurcations can be on-line detected. Near bifurcation points the Jacobian matrix plays a crucial role in the behavior of the underlying nonlinear ordinary differential equations (ODEs) [1]. Important kinetic information can be extracted from the Jacobian matrix (and its parameter dependence) [9–11]. The Jacobian matrix can be experimentally reconstructed [12,13] using pulse perturbations, concentration shift experiments, and closed-loop feedback control. Information about the reaction mechanism was obtained in the chlorite–iodide reaction [14,15], Belousov–Zhabotinsky reaction [16–18], and peroxidase–oxidase reaction [19,20].
In an alternative approach, relationships between system parameters can be obtained using bifurcation theory: in a heterogeneous CO oxidation reaction the parameter dependence of bistability was used to obtain information on the rate equation [21] and in electrochemical systems frequency relationships and dependence of oscillations on resistance, temperature, and rotation rate have been characterized [22–24]. Model development for distributed/coupled discrete systems were also accomplished: parameters for the complex Ginzburg–Landau equation were obtained from direct experiments to predict chemical waves in distributed systems [25] and phase models have been constructed to interpret synchronization and clustering of coupled chemical oscillator systems [26].

The application of invariant manifold technique [27–30] can greatly simplify the description of high-dimensional nonlinear ODEs which are strongly influenced by the presence of small parameters. In the simplest example of two variable ODE, there is often a small parameter (e.g., ratio of the timescales of the two variables) that results in one variable being fast, and the other variable being slow [31,32]. Therefore, the dynamics can be described as switching motion on the fast nullcline in state space. For example, in electrochemical models because of the time-scale separation of the electrode potential (fast variable due to fast double-layer charging) and the concentration of substances (slow variables), nullcline techniques have been successfully applied to interpret the existence of oscillations and multistationary behavior [33–36].

Nullclines in two-variable ODE systems are derived from the mathematical model equations. Motivated by the success of manifold/nullcline based theoretical analysis successes, experimentalists attempted to restrict behavior of complex nonlinear chemical systems to a lower dimensional state space using control engineering techniques. In heterogeneous surface reactions (e.g., CO oxidation on Pt) the relationships between steady state multiplicities under non-isothermal and isothermal (with temperature control) conditions were analyzed [37,38]. In photochemical reaction, external feedback was applied to investigate unstable states and transitions between stable states of a bistable reactor; in addition, bifurcations leading to oscillatory behavior were predicted [39]. In an electrochemical reaction, current–voltage relationships from potentiostatic control were used to interpret bistability under galvanostatic control in nickel electrodissolution [40].

In this paper, we propose a methodological approach for the extraction of nullcline information from direct experiments. In contrast to the traditional method that derives nullclines from existing ODEs, we apply a combination of control techniques using the fast and a slow variables. Because of the careful design of the control methodology, the stabilized system under the action of control will converge to points of the nullclines of the original (uncontrolled system). The methodology is extensively tested in numerical simulations of a general two-variable electrochemical model of electrochemical systems in three parameter regions where the systems exhibits oscillatory, bistable, and excitable behavior. In the numerical simulations we test the assumption that the nullcline points could be obtained with the use of experimental feasible control parameters, the circuit potential and rotation rate of the electrode. We also propose a technique by which a simple mathematical model could be constructed to predict the temporal variation of variables using the nullclines. In each region, the nullcline based model is analyzed for the number of predicted stationary states and features of typical trajectories. Finally, the limits of the method for obtaining nullcline with the control method is also demonstrated in an electrochemical model with three variables.

2. Material and methods

We apply the control technique to two ordinary differential equation models that are widely used for description of nonlinear behavior in electrochemical systems.

2.1. Two-variable model

A prototype model for oscillatory electrochemical systems was developed by Koper and Sluyters [41] and Koper and Gaspard [42]. Based on these models, a simple two variable model was previously used to develop quantitative relationships between system parameters that account for experimental observations [22,24,23,43]. The dimensionless model has two variables: fast variable electrode potential $e$ and slow variable near surface concentration $u$:

$$\frac{de}{dt} = \frac{V - e}{R} - 120k(e)u$$

$$\frac{du}{dt} = -1.25\sqrt{d}(e)u + \frac{4}{3}d(1 - u).$$

The major model parameters are the circuit potential $V$, cell series resistance $R$, and rotation rate of the electrode $d$. The rate constant $k$ depends on potential as

$$k(e) = 2.5\theta^2 + 0.01 \exp(0.5(e - 30))$$

where $\theta$ is related to the potential dependent surface coverage of a chemical substance

$$\theta = \begin{cases} 1 & \text{for } e \leq 35 \\ \exp[-0.5(e - 35)^2] & \text{for } e > 35. \end{cases}$$

For proper choices of $V$, $R$, and $d$ parameters the system could exhibit oscillations, bistability, or excitability [41].
2.2. Three-variable model

Many electrochemical processes involve more than two variables; for example, it was shown in metal activation/passivation processes, that a realistic model for the description of oscillatory waveform requires three variables [44]: electrode potential \( e \), near surface concentration of metal ions \( u \), and near surface concentration of hydrogen ions, \( h \). The model equations (in dimensionless form) are:

\[
\frac{de}{dt} = \frac{V - e}{R} - 100k_1^*(1 - \theta) \tag{3}
\]

\[
\frac{dh}{dt} = d(1.2 - h) - \frac{h}{1.2h + 0.4u} \sqrt{dV - e} \frac{1}{100R}
\]

\[
\frac{du}{dt} = -0.2du + \sqrt{d}(1 - \theta)k_1^* - \frac{0.2u}{1.2h + 0.4u} \sqrt{dV - e} \frac{1}{100R}
\]

where \( V \) is circuit potential, \( R \) is series resistance, \( d \) is rotation rate of the electrode, and \( \theta \) is surface coverage of the oxide film.

\[
\theta = \frac{1}{1 + 0.1h \exp[-(e - 20)]}
\]

The rate constant \( k_1^* \) is given as

\[
k_1^* = 0.01 \exp(e/2) \left( 1 - \frac{u}{-0.5h + \sqrt{0.25h^2 + 16}} \right).
\]

Similar to the two-variable model the major experimental parameters are \( V, R, \) and \( d \).

Both the two- and the three-variable models were integrated using software XPP [45].

3. Results and discussions

3.1. Theory

Consider a 2-variable dynamical system, which is described by variables \( x \) and \( y \)

\[
\varepsilon \frac{dx}{dt} = f(x, y, p) \tag{4}
\]

\[
\frac{dy}{dt} = g(x, y, q)
\]

where \( t \) is time, \( \varepsilon \ll 1 \) is a small parameter that makes \( x \) a fast variable and \( y \) a slow variable. The parameters \( p \) and \( q \) are used to affect the shape of nonlinear functions \( f \) and \( g \). Nullcline of variable \( x \) is defined [1] as

\[
f(x, y, p) = 0
\]

while the nullcline for variable \( y \) is

\[
g(x, y, q) = 0.
\]

The nullclines thus give a relationship between the variables of the system where there is no temporal change of a specific variable. The nullclines are usually plotted in the state space \( (x, y) \) after which a geometric analysis is performed about the dynamical behavior of the system.

We propose a control based approach for obtaining the nullcline points without a priori knowledge of function \( f \) and \( g \). Consider first obtaining the \( x \) nullcline points, i.e., relationships for \( f(x, y, p) = 0 \) at a given value of control parameter \( p = p_0 \). First assume that a robust controller is used, which will fix the variable \( y \) to a constant value, \( y^* \). (We shall discuss this control problem below.) Now Eq. (4) is a one-dimensional ordinary differential equation:

\[
\varepsilon \frac{dx}{dt} = f(x, y^*, p).
\]

The nullcline points that correspond to \( y^* \) at \( p = p_0 \) are the steady state solutions of Eq. (6). The values of these steady state solutions can be obtained with an adaptive controller [8,4] with perturbations \( \delta p \) of parameter \( p = p_0 + \delta p \):

\[
\delta p = L(w - x)
\]

\[
\frac{dw}{dt} = \lambda(w - x)
\]
where \( w \) is an external control variable, \( L \) is control gain, and \( \lambda \) is a control variable that defines a time scale at which \( w \) traces the \( x \) variable. The stable part of the nullcline is easy to obtain even without the adaptive control \((L = 0)\). If the unstable part of the nullcline translates into unstable node or focus (or in general, steady state with even number of positive eigenvalues), the system can be controlled with stable controller \((\lambda < 0)\); similarly, unstable saddles type stationary state (or steady states with odd number of positive eigenvalues) can be controlled with unstable controller \((\lambda > 0)\). Nonetheless, it was demonstrated \([8,4]\) that this control approach is a useful technique to obtain unknown stationary states of dynamical systems.

Now we consider the control problem of setting the \( y \) variable to a preset value \( y^* \). This is a traditional control problem and can be generally attained with proportional–integrative–derivative (PID) controller \([46]\) in which a suitable chosen control parameter \((q \in \text{our example})\) is perturbed as

\[
\delta q = \alpha(y - y^*) + \beta \frac{dy}{dt} + \gamma \int_0^t (y(\tau) - y^*) \, d\tau
\]

where \( \alpha, \beta, \) and \( \gamma \) are control parameters that correspond to the proportional, derivative, and integral terms, respectively. The proper choice of control parameters \([46]\) can be achieved using repetitive optimizations algorithms, however, because of the simplicity of the algorithm the parameters can be adjusted by intuitive trial-and-error parameter search.

In summary, we can see that successful, simultaneous applications of the PID controller with setpoint \( y^* \) using parameter \( q \) and adaptive controller with variable \( x \) and parameter \( p \) give stabilized steady states \( x^* \) that correspond to the \( x \) nullcline points of the original system equations \((4) -(5)\). (There could be more than one steady states because of multiplicity of the nullcline curves.) Mapping out several steady states at a given \( y^* \) requires integration from different initial conditions and testing different (stable and unstable) control parameters as it is often done in numerical explorations of ordinary differential equation models. The nullcline points for the \( y \) variable can be conveniently obtained by switching the controller variables: combination of PID control in variable \( x \) with setpoint \( x^* \) using parameter \( p \) and adaptive control in variable \( y \) with control parameter \( q \) then results in steady states (nullcline points) of the corresponding \( y \) variable.

### 3.2. Results with two-variable ODE model

The control based methodology for obtaining nullclines is implemented for the two-variable model equations \((1) -(2)\).

#### 3.2.1. Model of oscillatory behavior

Consider system parameters \( V = 36.9778, R = 0.023, d = 0.11913 \). Without any control the system exhibits periodic oscillations of variables \( e \) and \( u \) shown in Fig. 1(a) and (b) for \( t < 0 \). Note that for the fast variable \( e \) the waveform consists of time frames of slow variations and quick jumps; in contrast, for the slow variable \( u \) such a distinction is not possible.

In order to obtain nullcline points for the \( e \) variable the general methodology presented in Section 3.1 shall be adopted for the numerical model. A suitable control parameter for \( e \) variable is the circuit potential, \( V \). The parameter \( V \) shall be adjusted using variable \( e \) with the adaptive controller as follows:

\[
V = V_0 + L(w - e)
\]

\[
\frac{dw}{dt} = \lambda(w - e)
\]

where \( V_0 \) is a set potential at which the nullcline points are sought. For PID control of concentration \( u \) we have chosen the rotation rate of the electrode \( d \). Therefore, the rotation rate is set as

\[
d = d_0 + \alpha(u - u_0) + \beta \frac{du}{dt}
\]

where \( d_0 \) is the rotation rate at which the system is being investigated and \( u_0 \) is the setpoint. Note that we do not consider the integral component in the PID algorithm for simplicity. As we show below, this simplified algorithm was sufficient in the given application. The combined control algorithm (Eqs. \((9) \) and \((10)\)) works very efficiently in suppressing the oscillations. Fig. 1(a) and (b) show the stabilizing effect of the stable adaptive control \((\lambda = -0.1, L = 1)\) and a proportional control \((\alpha = -0.1, u_0 = 0.5, \beta = 0)\) for \( t > 0 \). The proportional term in Eq. \((10)\) is sufficient for suppressing the oscillations (the derivative term is not necessary). Because of the omission of the integrative term in Eq. \((10)\), there is an error between the expected value of the \( u \) variable \((0.5)\) and the stabilized value \( u = 0.2831 \). This common problem of the PID controller \([46]\), however, does not cause any difficulty since we can use the stabilized value of the \( u \) variable for the nullcline point instead of the setpoint.

When the setpoint is changed between 15 and \(-0.85\), the entire nullcline could be obtained with the control parameters as shown in Fig. 1(c). For comparison, the theoretical nullcline is also plotted, which is obtained from Eq. \((1)\) as

\[
u = \frac{V - e}{120Rk(e)}
\]

The figure shows that the control algorithm without knowledge of system equations gives the same nullcline points as one could obtain it from the mathematical equation.
Fig. 1. Obtaining nullcline points using the control algorithm in the 2D model. Top row: The oscillatory behavior is suppressed by combination of adaptive control in variable $e$ using parameter $V$ and PID control in variable $u$ using parameter $d$. The control is turned on at time $t = 0$ with parameters $\lambda = -0.1, L = 1, \alpha = -0.1, u_0 = 0.5, \beta = 0$. a. Variable $e$ vs. time. b. Variable $u$ vs. time. Bottom row: Theoretical nullclines (solid lines) and nullcline points obtained with control algorithm (markers). c. The $e$ nullcline points obtained with $\lambda = -0.1, L = 1, \alpha = -0.1, \beta = 0$. The $u_0$ parameter was varied between 15 and -0.85. d. The $u$ nullcline points obtained with adaptive control in variable $e$ using parameter $d$ and PID control in variable $u$ using parameter $V$. $\lambda = -0.1, L = 1, \alpha = -0.15, \beta = -0.36$. The $e_0$ parameter was varied between 0.5 and 80. System parameters: $V_0 = 36.9778, R = 0.025, d_0 = 0.11913$.

A similar algorithm was implemented for obtaining the $u$ nullcline. An adaptive controller is used in variable $u$ with parameter $d$

$$d = d_0 + L(w - u)$$

$$\frac{du}{dt} = \lambda(w - u).$$

A PID controller is in variable $e$ with parameter $V$

$$V = V_0 + \alpha(e - e_0) + \beta \frac{de}{dt}.$$

The nullcline points obtained with the control are shown in Fig. 1(d) with control parameters $\lambda = -0.1, L = 1, \alpha = -0.15, \beta = -0.36$. Note that for successful stabilization the derivative controller needed to be applied. The obtained points are the same as the theoretical $u$ nullcline derived from Eq. (2)

$$u = \frac{2}{2 + \frac{15}{\sqrt{d}}} k(e).$$

Once nullclines are obtained for the system, various features of the dynamical behavior could be predicted. Fig. 2(a) shows the $e$ and $u$ nullclines. The nullclines intersect at one point giving one (unstable) steady state. When the system is started from an initial condition such as shown in point A, the variation of $e$ will be much faster than the variation of $u$ and the system will be directed in phase space toward point B on the $e$ nullcline because $de/dt < 0$. Once the trajectory hits the $e$ nullcline (point B) $de/dt \approx 0$, thus the value of $du/dt$ determines the behavior. Because $du/dt < 0$, the variable $u$
Fig. 2. Nullcline analysis of 2D model and waveform prediction in oscillatory region. a. The e (thin curve with triangles) and the u (thin curve with squares) nullcline, an oscillatory cycle (thick curve), and nullcline model prediction (arrows). Markers are nullcline points obtained from control simulations. b. Oscillatory waveform from numerical solution (solid markers) and nullcline model prediction (open markers). For oscillatory waveform Eq. (12) is used with $K = -1.335$ between points F–C, and $K = -0.421$ between D–E. System parameters are the same as in Fig. 1.

decreases and the variable $e$ is quickly adjusted to follow the $e$ nullcline. Therefore, the phase point moves toward point C, which is at the local minimum of the $e$ nullcline. At this point, the $u$ variable slightly decreases, and since $\frac{de}{dt} > 0$, the system quickly jumps to point D on the $e$ nullcline. At point D $\frac{du}{dt} > 0$, therefore, the system moves along the $e$ nullcline until point E (local maximum of the $e$ nullcline) where another quick transition occurs to point F because $\frac{de}{dt} < 0$. The cycle then continues between points F–C–D–E. The validity of this prediction is confirmed by numerical simulation of the trajectories.

The nullcline model is well suited for the analysis of trajectories in the state space $e$ vs. $u$, however, the rate at which the phase point travels along a trajectory is not given. In order to construct a simple model from nullcline based analysis, we propose an approximate method for reconstruction of trajectories. When the system is off the nullcline of the fast variable $e$, the phase point instantaneously seeks the $e$ nullcline. When motion occurs on the $e$ nullcline, we can approximate the dynamics of the $u$ variable with a first order approximation:

$$\frac{du}{dt} = K(u - u_{nc}(e))$$

(11)

where $u_{nc}(e)$ is the $u$ value of the $u$ nullcline at the present value of the fast variable $e$ and $K$ is a proportionality constant. Eq. (11) is certainly an approximation; for complete description higher order terms may be needed. Nonetheless, we found that $K$ values obtained from the fit of $\frac{du}{dt}$ as a function of $u - u_{nc}(e)$ give a reasonable reconstruction of system dynamics.
3.2.2. Nullcline based model in bistable region

We also tested the applicability of the control based methodology for model building in parameter region where bistability occurred. In this region, new challenges in implementing successful control occurred. Results for obtaining the $e$ nullcline points are shown in Fig. 3(a)–(b). When a stable adaptive controller is applied two distinct $e$ nullcline points could be obtained for the same $u_0$ values as shown in 3(a). In this $u_0$ range when the unstable adaptive controller is turned on, an additional, third nullcline points are stabilized forming a classical inverted S-shaped bifurcation diagram. Nonetheless, as shown in Fig. 3(b), the control based and theoretical nullcline points are the same. Such a problem did not occur with the reconstruction of the $u$ nullcline points; the only complication was that a strong derivative controller needed to be applied at intermediate values of $e_0$ to suppress oscillations that were apparently introduced by the proportional controller. (Note that in this region adaptive controller was not needed for the control.)
Fig. 4. Nullcline model predictions for transitions between stable steady states of the 2D model using small perturbations in the bistable region. \((V_0 = 39.0696, R = 0.0713, d = 0.11913)\) Top panel: Nullcline analysis showing the transition between neighborhood of one stable steady state to another steady state. Thick solid line: B to A. Thick dashed line: A to B. The \(e\) and \(u\) nullclines are denoted with thin solid and dashed lines, respectively. Bottom panels: Comparison of numerical simulations of model equations (solid lines) and nullcline predictions (dashed lines) for the transition between steady states. b. Transition from perturbation of steady state B to A. \((K = -1.335)\) c. Transition from perturbation of steady state A to B. \((K = -0.421)\).

In the multistable region the nullclines can predict the number and stability of steady states. The three intersections of the \(e\) and \(u\) nullclines give three steady states: two of which are stable and one is unstable. In the bistable region the two stable steady states are only locally stable. Proper small perturbation can induce transitions between the two stable steady states A and B (see Fig. 4). These transitions follow the nullcline based state space predictions as they consist of nearly horizontal lines of approaching the \(e\) nullclines and movement along the \(e\) nullclines to the stationary states. The trajectories for the transitions are adequately reproduced with Eq. (12) as shown in Fig. 4(b)–(c). (Note that because the \(u\) nullclines do not depend on parameters \(V\) and \(R\), we can use the same \(K\) values obtained in the oscillatory region in Eq. (12).)

3.2.3. Nullcline based model in excitable region

Nullclines were also obtained using the control approach in excitable region \((V_0 = 36.45, R = 0.5845, d = 0.11913)\). The \(e\) nullclines can be obtained with adaptive–proportional controller as shown in Fig. 5(a)–(b). The \(u\) nullcline did not require adaptive control; at low and high \(e_0\) values simple proportional control was sufficient, however, the middle part of the nullcline is very difficult to stabilize and a PID controller was used with a very strong derivative component (see Fig. 5(c)–(d)). The \(e\) and the \(u\) nullclines have one intersection giving a stable steady state. This steady state is stable against small positive perturbations of the \(e\) variable, however, when a small negative perturbation is applied which crosses the \(e\) nullcline the \(e\) variable quickly decreases until the left branch of the \(e\) nullcline is reached, and gives an oscillatory cycle similar to that shown in Section 3.2.1. As shown in Fig. 5, the excitatory cycle is well reproduced using Eq. (12).

3.3. Results with three-variable ODE model

The nullcline technique is primarily used for two-variable model where there is clear separation of timescales between the variables. However, during the experimental exploration of the dynamical system, the number of essential variables may not be known. We consider an example of iron dissolution, in which in addition to the fast \(e\) and slow \(u\) variables, an
Fig. 5. Nullcline model construction and test of prediction for supra-threshold perturbation of the 2D model in the excitable region of parameters. \( (V_0 = 36.45, R = 0.5645, d = 0.11913) \) Top row: Obtaining the \( e \) nullcline points with control algorithm. a. Stabilized values of \( e \) vs. control parameter \( u_0 \). For the low and high potential branch (Proportional control) \( L = 2, \alpha = 0.1, \beta = 0, \lambda = -0.1 \). b. Nullcline curves obtained from data in panel a plotted in \( e \) vs. \( u \) plane. (Thin lines are the theoretical \( e \) (solid) and \( u \) (dashed) nullclines.) Middle row: Obtaining the \( u \) nullcline points with control algorithm. c. Stabilized values of \( u \) vs. control parameter \( e_0 \). For the low and high potential branch (Proportional control) \( L = 0, \alpha = 0.1, \lambda = -0.1, \beta = 0 \). For the middle potential branch (PID control) \( L = 0, \alpha = 0.1, \lambda = -0.1, \beta = -25 \). d. Nullcline curves obtained from data in panel c plotted in \( e \) vs. \( u \) plane. (Thin lines are the theoretical \( e \) (dashed) and \( u \) (solid) nullclines.) Bottom row, panel e: Nullcline model predictions for time dependence of \( e \) for a supra-threshold excitation calculated with Eq. (12) with the same \( K \) values as in Fig. 2.

additional essential species also exists in the form a slow \( h \) variable in Eq. (3). Nonetheless, without knowledge about the existence of this variable, one could 'blindly' apply our control to obtain for example the \( e \) nullcline and attempt to make predictions about the dynamics in the \( e \) vs. \( u \) parameter space.
We consider a parameter region where the system is oscillatory without control \((V = 30, R = 1, d = 1)\) as shown in Fig. 6(a)–(b). During implementation of control algorithms through Eqs. (7)–(8) we found a limitation that the rotation rate \(d\) reached very small values; because of the small imposed changes of \(u\) values the proportional controller could not induce effective variations of the rotation rate. To overcome this limitation, we applied a modified formula for the PID controller in which the exponential of the difference (multiplied with a control gain) between \(u\) and the setpoint \(u_0\) is used in controlling the rotation rate:

\[
d = d_0 + \exp[\alpha(u - u_0)] + \beta \frac{du}{dt}.
\]

This modified equation could successfully control the system and the obtained ‘nullcline’ points are shown in Fig. 6(c). The use of this curve becomes imminent when the oscillatory cycle is overlaid in the \(e\) vs. \(u\) state space: the limit cycle traces the stable branches of the obtained curve (see Fig. 6(d)) just as it did with the actual two-variable model. This result is not trivial to interpret: it is likely that the system exhibits a manifold in which the \(u\) and \(h\) variables are functionally related and thus the limit cycle behavior can be explained in the \(e\) vs. \(u\) state space. This assumption can be supported by the simulation results that the nullcline points can also be obtained by using \(h\) variable in PID controller in Eq. (13); some control based nullcline points are shown in circles using this technique in Fig. 6(d). The extension of the methodology to high dimensional systems with existing multi-dimensional manifolds is an important future goal for the model development.

4. Conclusions

A model-free methodology was presented to obtain nullclines of a system with a systematic feedback control methodology. The methodology was demonstrated to successfully reproduce nullcline curves in a two-variable model for electrochemical systems. Based on nullcline information, a simple model was built to reconstruct time dependence of phase
space trajectories. The success of the method implies that in electrochemical systems where time-scale separation exists, the nullclines can be extracted from direct experiments by measuring the electrode potential (by current measurements) and near surface concentration (by additional electroanalytical techniques, e.g., ring current measurements) and by controlling of the system with circuit potential and rotation rate. There is indirect experimental information that the relaxation oscillations in copper electrooxidation can be interpreted with nullcline technique [24], therefore, the reaction is good target for an experimental test. However, the methodology is not restricted to electrochemical systems, and holds promise, for example, in building simple yet accurate models for biological systems that could be used in building large-scale models in systems biology. Another expansion of the technique could be in the direction of construction of general manifolds instead of the traditional nullclines.

Acknowledgments

An acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund and the President’s Research Fund of Saint Louis University for support of this research.

References


