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Note

Multistationarity is neither necessary nor sufficient to oscillations

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The existence of more than one stationary point for certain parameter values is generally considered to be a necessary condition of the emergence of oscillatory solutions for some parameter values in reaction kinetics. Examples taken from both physics and chemical kinetics show that the condition is neither necessary nor sufficient.

1. Introduction

The theory of reaction kinetics is full with tradition, beliefs, conjectures and refutations. Let us mention just a few of them. Reversible reactions have a positive stationary concentration (true [28]), they only have one (false [7]). “Closed sytems tend to equilibrium” – if this statement is meant to mean that reversible detailed balanced reactions have a single, locally relatively asymptotically stable stationary point, then it is true [17,31,35] and has also been generalized to the case of complex balanced reactions [13,14,19,20]. Autocatalytic, autoinhibitory, or enzymatic steps are needed to obtain oscillatory reactions [2,23], false [22], cf. also [29]. Feed-back is needed to oscillation [5]. (It was even possible to produce chaos with mono- and bimolecular steps without autocatalysis [24].) A more detailed account of history from this aspect can be found in [11, section 4.2].

In this short note we consider the statement (or, rather, conjecture) according to which multistationarity is a necessary or sufficient condition of oscillation in complex chemical reactions [3,6,10]. More precisely, the assertion is that in order to have periodic solutions in a complex chemical reaction at *some* values of the parameters, the reaction *must* have more than one stationary point for some values of the parameters. The majority of model reactions (as, e.g., the Autocatalator, the Ivanova reaction, the Lotka–Volterra reaction, the Oregonator) have this property. What is more, real chemical systems with oscillatory behavior also share this property and they have partly been designed using this conjecture [9,30]. (Although the reaction of chlorite with thiocyanate exhibits oscillations without known bistability so far [1], and the ferroin-bromate system has been shown to produce bistability and no oscillation until no bromide was added [16].)

As Li and Wu put it [26]: "... cross-shaped phase diagram analysis ... which starts with a search for bistable systems has played an essential role."

The debate about the Explodator [12,15,21,27] also focused on this conjecture: those against this model argued that the Explodator not being able to show bistability is not a viable model of any oscillatory reaction that exhibits bistability which includes nearly all of the presently known. The other party showed that the Explodator does show bistability at certain parameter values.

We shall present examples here to show that without additional requirements the statement in question is false in general, and we also show that the condition is not sufficient either. Finally, we also show that existence of a periodic solution in the given cases is a simple consequence of Poincaré–Bendixson theory.

2. Necessity

To investigate *necessity* let us start with the simple (nonkinetic) example of the harmonic oscillator:

$$\dot{x} = \omega y, \qquad \dot{y} = -\omega x.$$

This equation obviously has a periodic solution (for all initial values and) for all values of the parameter ω. It is also true that at a certain parameter value (namely, at $\omega = 0$) it shows multistationarity, because in this case all the points of the phase space turn out to be stationary points.

Modifying the example a bit, we obtain

$$\dot{x} = \left(1 + \omega^2\right)y, \qquad \dot{y} = -\left(1 + \omega^2\right)x.$$

This equation again has a periodic solution (for all initial values and) for all values of the parameter ω. Furthermore, it only has a single stationary point $(0, 0)$, no matter what the value of the parameter ω is.

Obviously, none of the two models above are kinetic because y is not directly involved in its own removal: the models contain negative cross-effect (see, e.g., [32,33] and the references therein). Still, the same trick will also help to construct kinetic models of a similar structure. Let us consider the reaction

$$\begin{aligned} &\mathcal{A} \to \mathcal{X}, \qquad \mathcal{X} + \mathcal{Z} \to \mathcal{B}, \qquad \mathcal{Y} \to \mathcal{Y} + \mathcal{Z}, \\ &\mathcal{X} \to \mathcal{X} + \mathcal{Y}, \qquad \mathcal{Y} + \mathcal{W} \to \mathcal{C}, \qquad \mathcal{D} \to \mathcal{W}, \end{aligned}$$

constructed by Dancsó and Farkas as a simple chemical realization of the harmonic oscillator [4]. A dimensionless form of its induced kinetic differential equation is

$$\begin{aligned} \dot{x} &= a(1 - xz), \qquad \dot{y} = b(x - yw), \\ \dot{z} &= c(y - xz), \qquad \dot{w} = d(1 - yw). \end{aligned}$$

This equation (having oscillatory solutions) again has the property that for some values of the parameters (namely for $a = b = c = d = 0$) it has more than one stationary point.

However, reparametrizing the equations in the same way as above we obtain

$$\dot{x} = \big(1+\alpha^2\big)(1-xz), \qquad \dot{y} = \big(1+\beta^2\big)(x-yw),$$
$$\dot{z} = \big(1+\gamma^2\big)(y-xz), \qquad \dot{w} = \big(1+\delta^2\big)(1-yw),$$

a counterexample, having the single stationary point $(1,1,1,1)$.

A less trivial, more chemical exmple can be created from the two-variable model of the *chlorite iodide malonic acid* (CIMA, for short) reaction [25]:

$$\dot{x} = k_1 - k_2x - 4k_3\frac{xy}{u+x^2}, \qquad \dot{y} = k_2x - k_3\frac{xy}{u+x^2},$$

if one puts $k_i := 1+\omega_i^2$ $(i = 1,2,3)$ and $u := 1+\Omega^2$. Obviously, the single stationary point is

$$x^* = \frac{1+\omega_1^2}{5(1+\omega_2^2)}, \qquad y^* = \frac{1+\omega_2^2}{1+\omega_3^2}\left(1+\Omega^2+\left(\frac{1+\omega_1^2}{5(1+\omega_2^2)}\right)^2\right).$$

3. Sufficiency

Multistationarity alone is not *sufficient* to imply oscillation either. This is trivially true for one-dimensional systems as they cannot oscillate although they can have any number of stationary points.

However, an artificial example like the induced kinetic differential equation

$$\dot{x} = (x-a)(x-b)y, \qquad \dot{y} = x(y-c)(y-d)$$

of the reaction

$$2\mathcal{X}+\mathcal{Y} \xrightarrow{1} 3\mathcal{X}, \qquad \mathcal{X}+2\mathcal{Y} \xrightarrow{1} 3\mathcal{Y},$$
$$\mathcal{A}+\mathcal{Y} \xrightarrow{ab} \mathcal{X}+\mathcal{Y} \xrightarrow{a+b} \mathcal{Y}+\mathcal{B},$$
$$\mathcal{A}+\mathcal{X} \xrightarrow{cd} \mathcal{X}+\mathcal{Y} \xrightarrow{c+d} \mathcal{X}+\mathcal{B}$$

shows that even a system with five stationary states can do without being oscillatory: all the coordinates of all the nonconstant solutions are always strictly monotonous in this case.

4. Closing remarks

Finally, let us mention that in the case investigated by Li and Wu [26] the single stationary state is not only unstable, but it is also a *source*, an unstable stationary point with the real parts of all the eigenvalues being positive numbers. This makes it possible to define an annulus on the phase plane such that the trajectories come into this both from the part of the state space outside the annulus and from the neighborhood of the unstable stationary state. Thus, standard application of the Poincaré–Bendixson theory [18, p. 247] implies the existence of a periodic solution in this case without any reference to multistationarity.

An analogous new and interesting (heuristically founded) conjecture to the one treated here has been put forward by Li and Wu [26]: A complex chemical reaction showing bistationarity when completely stirred (i.e., under homogeneous conditions) might be able to produce spatial patterns when diffusion is taken into consideration. We cannot either prove or disprove this statement at the moment. However, we have been able to *prove* (and extend in some sense) the seemingly obvious statement that *nonlinearity* is a necessary condition of the appearance of Turing structures [32]. (Thus we also contributed to the clarification of the statement by Epstein [8] saying that "Turing ... showed that a sufficiently nonlinear set of reaction kinetics coupled to diffusion could give rise to pattern formation ..."; false, Turing constructed a *linear, nonkinetic* example in his seminal paper [34].)

Summary and conclusion of the story by a self-content mathematician would be: These chemical physicist guys simply used a nonexistent theorem. A more modest mathematician's summary might be: The strong relation between this nonexistent theorem and both experimental and model results should force us to look behind the new idea ("from bistability to spatial patterns") and try to prove or disprove it, or try to add some further conditions under which the statement will become true in the mathematical sense too.

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