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On the possibility of
spontaneous
chemomechanical oscillations
in adsorptive porous media

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We derive general conditions for the emergence of sustained chemomechanical oscillations from a non-oscillatory adsorption/desorption reaction in a gas/solid porous medium. The oscillations arise from the nonlinear response of the solid matrix to the loading of the adsorbed species. More particularly, we prove that, in order for oscillations to occur, adsorption of the gas must in general cause a swelling of the solid matrix. We also investigate the prototypical case of Langmuir kinetics both numerically and analytically.

This article is part of the theme issue 'Dissipative structures in matter out of equilibrium: from chemistry, photonics and biology (part 2)'.

1. Introduction

Fifty years ago, Prigogine & Lefever [1] proposed the simple abstract model of a chemical oscillator now known as the Brusselator. It is difficult to overstate the role that the Brusselator has had in the development of nonlinear chemical dynamics. In the years that followed, other simple oscillatory models, some of them, such as the Oregonator [2], based more directly on specific chemical oscillators, were developed and led to important insights into the phenomenology of nonlinear chemical reaction networks.

These models, and most early experimental studies of chemical oscillation, focused on homogeneous systems, typically in aqueous solution, though both experiments

and models were subsequently extended beyond well-stirred systems to include the waves and patterns that arise in reaction–diffusion systems.

In the half century following the birth of the Brusselator, investigations of chemical oscillation and pattern formation have increasingly turned toward heterogeneous media, where the necessary nonlinearity in the dynamics may arise primarily from the kinetics of the chemical reaction network, the behaviour of the medium or the interaction of the two. For example, experiments on beads of cation exchange resin impregnated with the catalyst of the Belousov–Zhabotinsky (BZ) reaction in a solution of the BZ reactants [3] or on microemulsions consisting of the BZ components in aqueous nanodroplets surrounded by a monolayer of surfactant in a sea of octane [4] give rise to a much richer array of dynamical behaviour than the BZ reaction in homogeneous aqueous solution. In these systems, the chemistry of the BZ reaction provides the essential nonlinear dynamics, and the medium enables inherently oscillatory subunits to interact in novel ways. On the other hand, in experiments involving relatively simple reactions, such as the oxidation of carbon monoxide on metal surfaces [5], changes in the character of the surface in response to changes in surface coverage by reactants and intermediates constitute the major impetus for the wealth of patterns observed. Similarly, in gels one may contrast the behaviour of oscillatory BZ gels, pioneered by Yoshida [6], in which the BZ dynamics drive the remarkable chemomechanical behaviours observed, with the systems studied by Boissonade [7] and Horvath *et al.* [8], in which a mildly nonlinear (spatially bistable, but not oscillatory) kinetics interacts with a pH-responsive gel medium so as to generate chemomechanical oscillations.

In this paper, we explore whether extremely simple chemistry, i.e. adsorption and desorption of a single chemical species onto a porous solid whose porosity varies nonlinearly with surface coverage, can result in oscillations. In our treatment, only one reversible elementary chemical reaction step is involved, and complicated chemical feedbacks such as those encountered in the BZ reaction are excluded. We develop and analyse a two-variable model for such a system, which one might dub the ‘poroscillator’, and demonstrate that oscillations can in fact arise under appropriate conditions. We first describe the elements of the model and the corresponding set of rate equations in a rather general way. This allows us to derive the broad conditions under which the model might allow oscillations. We then turn to the specific case of Langmuir kinetics subject to different functional dependences of the porosity on the surface coverage. We use our theory to prove that while linear porosity functions are unable to destabilize the steady state, nonlinear porosities can indeed produce oscillations under appropriate conditions. We numerically test these last results by choosing a sigmoidal porosity function.

2. Theory in terms of surface concentration

Let us consider a system where a solid porous matrix of volume V_s is continuously and uniformly in contact with a gas phase of volume V_g . We assume that the gas phase contains a reactive species X at molecular concentration C , which can reversibly adsorb on specific adsorption sites on the surface of the solid matrix, whose total number per unit surface area of solid is σ^\dagger . We define the fraction of adsorption sites occupied by the species X as the coverage θ and the surface concentration of X molecules as $\sigma = \theta\sigma^\dagger$. We are interested in the case where the structural properties of the solid matrix are modified by the presence of the adsorbed gas. More particularly, we assume that the solid matrix can reversibly swell when molecules of X are either adsorbed or desorbed, thus increasing the volume V_s .

Our first aim is to derive suitable evolution equations for C and σ . If we denote by v_{ads} and v_{des} the molecular rates of adsorption and desorption—i.e. the number of gas molecules per unit time that, respectively, adsorb onto or desorb from a unit surface of the solid matrix—we can write

$$\frac{d\sigma}{dt} = v_{\text{ads}} - v_{\text{des}}. \quad (2.1)$$

In order to derive a similar equation for C , we consider that, although V_s and V_g may vary because of the adsorption reaction, the total volume $V_t = V_s + V_g$ of the system—which is assumed to

reside in a rigid container—is constant. If we define the porosity of the system as $\phi = V_g/V_t$, the quantity ϕC can only vary due to changes in the number of molecules of X in the gas phase, which—in a closed system—only occur because of the adsorption/desorption reaction with the solid matrix. The mass balance on the molecules of X in the volume V_t will therefore read

$$\frac{d(\phi C)}{dt} = -\frac{d(\zeta \sigma)}{dt} = -\zeta(v_{\text{ads}} - v_{\text{des}}) - \sigma \frac{d\zeta}{dt}, \quad (2.2)$$

where ζ is a specific surface area, i.e. the area of solid matrix divided by the total volume V_t .

Notice that when we expanded the derivative on the RHS of the previous equation, we had to account for the fact that the specific surface area ζ can change in time because of the swelling of the matrix. In a similar way, we cannot consider the porosity ϕ as constant in time when calculating the time derivative of the LHS of equation (2.2), due to the fact that we assumed that V_s varies with σ while V_t remains constant. This will therefore produce a term proportional to $d\phi/dt$ for which, together with the term $d\zeta/dt$, we should in principle provide additional evolution laws. This task can be properly performed only if we know how the mechanical properties of the solid matrix relax in time in response to a change in composition, but such a detailed analysis is beyond the scope of this paper. Our aim here is to investigate the possibility of identifying a mechanochemical coupling that can lead to sustained oscillations with minimal ingredients; therefore, we wish to keep our model as simple as possible. For this reason, we assume that we can take all structural properties of the solid matrix to be functions of the coverage, whose precise form is, of course, system dependent, but which nevertheless allows us to invoke the chain rules $d\phi/dt = (\partial\phi/\partial\sigma)(d\sigma/dt)$ and $d\zeta/dt = (\partial\zeta/\partial\sigma)(d\sigma/dt)$. One way to realize this is, for example, if the relaxation of the solid matrix to a new configuration due to composition changes occurs on a much faster time scale than that of the reaction. Using the chain rule, we can write equation (2.2) as

$$\frac{dC}{dt} = -\left[\left(\varepsilon + \frac{\partial\varepsilon}{\partial\sigma}\sigma\right)\frac{1-\phi}{\phi} + (C - \varepsilon\sigma)\frac{\partial\ln\phi}{\partial\sigma}\right](v_{\text{ads}} - v_{\text{des}}), \quad (2.3)$$

where we have additionally expressed the specific surface area as $\zeta = \varepsilon(1 - \phi)$, with ε being the ratio between the surface and the volume of the solid matrix.

Equations (2.1) and (2.3) describe a closed system, which will eventually reach a stationary state determined by the conditions for the chemical equilibrium of the adsorption/desorption reaction. In order to have sustained oscillations in time, we need to keep the system far from its equilibrium state by opening it to fluxes of matter (and/or energy). We therefore add to the RHS of equation (2.3) a term $\delta(C_0 - C)$, which models the effect of exchanging X at a constant flux rate δ with an external reservoir kept at constant concentration C_0 . The resulting equation describes a zero-dimensional or a “well-stirred” porous medium. A more detailed modelling approach would require the addition of a diffusion term to (at least) equation (2.3) and the introduction of exchanges with the external reservoir as boundary conditions. We do not expect, however, that such an extension of the present model would provide new qualitative insight with respect to the questions that are being assessed in this work. We shall therefore view this flux term as an approximation for infinitely large diffusion coefficients and understand that any instability that we may find in this homogeneous model may develop with a non-trivial spatial dependence when finite diffusion coefficients are taken into account.

So far we have kept the reaction rates v_{ads} and v_{des} rather general, but, in order to analyse the stability of the system, we need to know how these rates depend on the variables C and σ . For the sake of generality, we still avoid giving explicit expressions for the reaction kinetics at this stage and assume only that the desorption rate depends on the the surface concentration of adsorbed X molecules, while the adsorption rate also depends on the concentration of X in the gas phase. This assumption is reasonable if the gas phase is dilute in X and it is consistent with the most common adsorption/desorption kinetic laws. Introducing the rescaled concentration $c = C/C_0$, our system of equations can be written as

$$\frac{dc}{dt} = -\beta(c, \sigma)(v_{\text{ads}}(c, \sigma) - v_{\text{des}}(\sigma)) + \delta(1 - c) \quad (2.4)$$

and

$$\frac{d\sigma}{dt} = v_{\text{ads}}(c, \sigma) - v_{\text{des}}(\sigma), \quad (2.5)$$

with

$$\beta(c, \sigma) = \left(\frac{\varepsilon(\sigma)}{C_0} + \frac{\partial \varepsilon(\sigma)}{\partial \sigma} \frac{\sigma}{C_0} \right) \frac{1 - \phi(\sigma)}{\phi(\sigma)} + \left(c - \varepsilon(\sigma) \frac{\sigma}{C_0} \right) \frac{\partial \ln \phi(\sigma)}{\partial \sigma}, \quad (2.6)$$

and where we have highlighted the dependences of the possibly non-constant quantities on the dynamical variables.

We assume hereafter that, for any gas concentration, there is a single value of the surface coverage at which the adsorption and desorption rates are equal. Equations (2.4) and (2.5) therefore possess a unique steady state $(1, \sigma^0)$, where σ^0 is the solution of the balance condition $v_{\text{ads}}(1, \sigma^0) = v_{\text{des}}(\sigma^0)$. This is true, for example, for non-cooperative adsorption without intermolecular forces between adsorbates, or in the absence of phase transitions in the adsorbed phase. This restriction, however, does not affect the generality of our results even in the case of multistable systems.

In order to analyse the stability of the above steady state, we linearize equations (2.4) and (2.5) around it, obtaining the Jacobian matrix

$$J = \begin{bmatrix} -\beta(1, \sigma^0)(v_{\text{ads}})_c - \delta & -\beta(1, \sigma^0)((v_{\text{ads}})_\sigma - (v_{\text{des}})_\sigma) \\ (v_{\text{ads}})_c & (v_{\text{ads}})_\sigma - (v_{\text{des}})_\sigma \end{bmatrix}, \quad (2.7)$$

where all terms are evaluated at the steady state and where for simplicity of notation we have dropped the c and σ dependences and use a c or σ subscript to denote partial derivatives with respect to either variable. The signs of the trace

$$\text{Tr}(J) = -\beta(1, \sigma^0)(v_{\text{ads}})_c - \delta + (v_{\text{ads}})_\sigma - (v_{\text{des}})_\sigma, \quad (2.8)$$

and the determinant

$$\text{Det}(J) = \delta[(v_{\text{des}})_\sigma - (v_{\text{ads}})_\sigma], \quad (2.9)$$

of J determine the stability of the steady state. As shown below, $\text{Det}(J) > 0$, which implies that the steady state will become unstable for $\text{Tr}(J) \geq 0$, with the equal sign marking the onset of a Hopf bifurcation, typically associated with the creation of limit cycles and sustained oscillations.

Although we do not have explicit expressions for the kinetic laws in our model, we can still make educated guesses as to the signs of the derivatives in equations (2.8) and (2.9). The simplest scenario is when the rates of adsorption and desorption are monotonic functions of c and σ . Under this assumption, the rate of adsorption typically increases with the concentration of gas and decreases with the surface concentration of adsorbate. Similarly, the rate of desorption generally increases with the surface concentration of adsorbed species. From these considerations, we take

$$(v_{\text{ads}})_c > 0, \quad (v_{\text{ads}})_\sigma < 0, \quad (v_{\text{des}})_\sigma > 0. \quad (2.10)$$

Under conditions (2.10), $\text{Det}(J)$ is always positive regardless of the exact form of the kinetic laws. As for the trace, the last three terms in equation (2.8) are always negative under our assumptions and therefore act as stabilizing terms. The only source of instability can therefore come from the first term on the RHS of (2.8) if and only if $\beta(1, \sigma^0) < 0$. In order to see what this means in more explicit terms, we combine equation (2.8) with the inequality $\text{Tr}(J) \geq 0$ and rearrange to obtain

$$\left(1 - \varepsilon \frac{\sigma^0}{C_0} \right) (\ln \phi)_\sigma + \varepsilon \sigma \frac{\sigma^0}{C_0} \frac{1 - \phi}{\phi} \leq - \left[\frac{\varepsilon}{C_0} \frac{1 - \phi}{\phi} + \frac{\delta}{(v_{\text{ads}})_c} + \frac{(v_{\text{des}})_\sigma - (v_{\text{ads}})_\sigma}{(v_{\text{ads}})_c} \right]. \quad (2.11)$$

Expression (2.11) therefore provides a general condition that can be used as a test for both theoretical and experimental systems when the dependence of the solid structure on the composition is known or can be empirically determined.

3. Theory in terms of fractional coverage

Sometimes, it is more convenient to express the evolution equations in terms of the fractional coverage θ rather than the surface concentration σ . This is especially true if we want to derive explicit expressions for the control parameters of our system from simple microscopic arguments, because thinking in terms of fractional coverage and occupancy leads to much simpler geometric and kinetic arguments. This will be the case, for example, in the next section, when we explicitly introduce the Langmuir kinetics. Since our main purpose in switching to the θ framework is to have a more intuitive interpretation of the structure of our system, we first want to better quantify the relations between the structural parameters in our model, namely ϕ , σ^t and ε , by introducing a general geometric view of the microscopic structure of the system, which will allow us to introduce structural constraints in our kinetic model in a precise and controlled way.

Let us idealize the porous matrix as being composed of a collection of n_b blocks each of volume V_b and surface area A_b . Each block has on its surface a number n_s of adsorption sites, which is constant. For convenience, we develop our analysis in terms of the porosity variable. If we call V_{bM} the maximum volume that can be reached by each box—i.e. the volume for which all the space is filled with solid, or in other words $n_b V_{bM} = V_t$ —we can express the volume of each box as

$$V_b = V_{bM}(1 - \phi). \quad (3.1)$$

We also assume that, although the size of the blocks changes during adsorption, their shape does not. This ansatz allows us to write the surface to volume ratio and its derivative as

$$\varepsilon = \frac{A_b}{V_b} = \varepsilon_0 V_b^\gamma = \varepsilon_0 V_{bM}^\gamma (1 - \phi)^\gamma \quad (3.2)$$

and

$$\varepsilon_\sigma = \varepsilon_0 V_{bM}^\gamma (-\gamma)(1 - \phi)^{-1+\gamma} \phi_\sigma, \quad (3.3)$$

where ε_0 and γ are constants specific to the geometry of the blocks. In general, for non-fractal objects of regular shape, $\gamma = -\frac{1}{3}$ regardless of the shape, while ε_0 is shape dependent: for example, cubic boxes have $\varepsilon_0 = 6$, spherical boxes have $\varepsilon_0 = 6^{2/3}\pi^{1/3}$, etc. With this in mind, equation (3.3) shows that ε_σ and ϕ_σ have the same sign. Finally, we can use (3.2) to express σ^t and σ_σ^t in terms of ϕ ,

$$\sigma^t = \frac{n_s}{A_b} = \frac{n_s}{\varepsilon_0} V_{bM}^{-(1+\gamma)} (1 - \phi)^{-(1+\gamma)} \quad (3.4)$$

and

$$\sigma_\sigma^t = \frac{n_s}{\varepsilon_0} V_{bM}^{-(1+\gamma)} (1 + \gamma)(1 - \phi)^{-(2+\gamma)} \phi_\sigma. \quad (3.5)$$

The last equation, incidentally, shows that, if n_s is constant, σ_σ^t and ϕ_σ must have the same sign.

In order now to derive the evolution equations in terms of θ , we can either start from equations (2.1) and (2.2), assume that $\sigma^t = \sigma^t(\theta)$, $\varepsilon = \varepsilon(\theta)$ and $\phi = \phi(\theta)$, and follow a completely analogous reasoning to the one used to derive equations (2.4) and (2.5), or alternatively we can start directly from equations (2.4) and (2.5) and use the fact that $d\sigma = d(\sigma^t(\theta)) = \sigma^t(1 + \theta(\ln \sigma^t)_\theta) d\theta$ to transform all the derivatives with respect to σ into derivatives with respect to θ . In either case, we arrive at the following evolution laws for c and θ :

$$\frac{dc}{dt} = -\tilde{\beta}(c, \theta)(v_{\text{ads}}(c, \theta) - v_{\text{des}}(\theta)) + \delta(1 - c) \quad (3.6)$$

and

$$\frac{d\theta}{dt} = \frac{v_{\text{ads}}(c, \theta) - v_{\text{des}}(\theta)}{\sigma^t(\theta)(1 + \theta(\partial \ln \sigma^t(\theta)/\partial \theta))} \quad (3.7)$$

with

$$\tilde{\beta}(c, \theta) = \frac{\varepsilon(\theta)}{C_0} \frac{1 - \phi(\theta)}{\phi(\theta)} + \frac{(\theta/C_0)((1 - \phi(\theta))/\phi(\theta))(\partial \varepsilon(\theta)/\partial \theta) + (c/\sigma^t(\theta) - \varepsilon/C_0\theta)(\partial \ln \phi(\theta)/\partial \theta)}{1 + \theta(\partial \ln \sigma^t(\theta)/\partial \theta)}. \quad (3.8)$$

Comparison between equations (2.4), (2.5) and equations (3.6), (3.7) shows that they have a similar form, but the multiplying factors in the latter are more complicated than in the former. This is a consequence of explicitly expressing σ as the product of θ and σ^\dagger : as a result, the structural changes due to the swelling of the solid matrix are not only reflected in the change of porosity ϕ and surface to volume ratio ε , but also in the change of the total site density σ^\dagger . Similarly to what we did before, we can compute the Jacobian matrix J' of equations (3.6) and (3.7) around the steady state, $(1, \theta^0)$, which has trace and determinant

$$\text{Tr}(J') = -\tilde{\beta}(1, \theta^0)(v_{\text{ads}})_c - \delta - \frac{(v_{\text{des}})_\theta - (v_{\text{ads}})_\theta}{\sigma^\dagger(1 + \theta^0(\ln \sigma^\dagger)_\theta)} \quad (3.9)$$

and

$$\text{Det}(J') = \delta \frac{(v_{\text{des}})_\theta - (v_{\text{ads}})_\theta}{\sigma^\dagger(1 + \theta^0(\ln \sigma^\dagger)_\theta)}. \quad (3.10)$$

Now we assume that the rates of adsorption and desorption, respectively, decrease and increase with θ , so that

$$(v_{\text{ads}})_\theta < 0, \quad (v_{\text{des}})_\theta > 0. \quad (3.11)$$

Once again we find that, in order for the trace (3.9) to be positive, a necessary but not sufficient condition is that $\tilde{\beta} < 0$. However, in order to have a Hopf bifurcation now, we must also require that the denominator of equation (3.10) be positive—that is to say, $(\ln \sigma^\dagger)_\theta > -1/\theta^0$ —in order for $\text{Det}(J') > 0$; otherwise the steady state will be a saddle point. In more explicit terms, we can obtain sustained oscillations if

$$\begin{aligned} & \left(1 - \varepsilon \frac{\sigma^\dagger \theta^0}{C_0}\right) (\ln \phi)_\theta + \varepsilon \frac{\sigma^\dagger \theta^0}{C_0} \frac{1 - \phi}{\phi} (\ln \varepsilon)_\theta \\ & \leq - \left[\left(\frac{\varepsilon}{C_0} \frac{1 - \phi}{\phi} + \frac{\delta}{(v_{\text{ads}})_c} \right) \sigma^\dagger (1 + \theta^0 (\ln \sigma^\dagger)_\theta) + \frac{(v_{\text{des}})_\theta - (v_{\text{ads}})_\theta}{(v_{\text{ads}})_c} \right] \end{aligned} \quad (3.12)$$

and

$$1 + \theta^0 (\ln \sigma^\dagger)_\theta > 0. \quad (3.13)$$

Because of equations (3.2) and (3.4), we can express $(\ln \varepsilon)_\theta$ and $(\ln \sigma^\dagger)_\theta$ as

$$(\ln \varepsilon)_\theta = (-\gamma) \frac{\phi}{1 - \phi} (\ln \phi)_\theta \quad (3.14)$$

and

$$(\ln \sigma^\dagger)_\theta = (1 + \gamma) \frac{\phi}{1 - \phi} (\ln \phi)_\theta, \quad (3.15)$$

which simplifies equations (3.12) and (3.13) as

$$(\ln \phi)_\theta \leq - \left[\left(\frac{\varepsilon}{C_0} \frac{1 - \phi}{\phi} + \frac{\delta}{(v_{\text{ads}})_c} \right) \sigma^\dagger + \frac{(v_{\text{des}})_\theta - (v_{\text{ads}})_\theta}{(v_{\text{ads}})_c} \right] \left(1 + \frac{\delta \sigma^\dagger}{(v_{\text{ads}})_c} \frac{(1 + \gamma) \theta^0 \phi}{1 - \phi} \right)^{-1} \quad (3.16)$$

and

$$(\ln \phi)_\theta > - \left(\frac{(1 + \gamma) \theta^0 \phi}{1 - \phi} \right)^{-1}. \quad (3.17)$$

A careful look at equation (3.16) shows that the sums of the terms within square and round brackets are always positive, meaning that a necessary (although not sufficient) condition for $\text{Tr}(J)$ to be positive is that $(\ln \phi)_\theta$ must be strictly negative. This means that, in order to generate self-sustained chemomechanical oscillations from an adsorption/desorption reaction, the porosity must be a decreasing function of θ or, in other words, that adsorption of gas must cause a swelling of the solid matrix. This is a significant result, because it provides a strong restriction on the types of solid structures that can potentially produce this type of oscillation.

4. Langmuir kinetics

In order to gain more insight into the physical requirements needed to satisfy expression (2.11) or (3.16) and (3.17), we now introduce an explicit adsorption/desorption mechanism: Langmuir kinetics [9]. The main reason for this choice is that the Langmuir kinetics is arguably the simplest prototypical example of adsorption/desorption kinetics. This system will therefore provide a useful benchmark to assess the conceptual validity of the theory we propose here, while at the same time serving as a minimal example for possible future investigations. In other words, if the recipe we propose here is able to generate oscillations with Langmuir kinetics, it is even more likely that oscillations will arise when more complex kinetic laws are considered.

The rates of adsorption and desorption for Langmuir kinetics can be expressed as

$$v_{\text{ads}} = k_{\text{ads}} C_0 \sigma^t c (1 - \theta) = k_{\text{ads}} C_0 c (\sigma^t - \sigma) \quad (4.1)$$

and

$$v_{\text{des}} = k_{\text{des}} \sigma^t \theta = k_{\text{des}} \sigma, \quad (4.2)$$

where k_{ads} and k_{des} are two kinetic parameters whose values depend on the temperature and on the chemical nature of the system, but which are assumed to be constant with respect to both the adsorption/desorption reactions and the expansion/contraction of the solid matrix. In order to rigorously verify this assumption in microscopic terms, one can explicitly derive equations (4.1) and (4.2) from the kinetic theory of gases [10] and show that the microscopic quantities defining the two kinetic constants are not affected by the swelling of the solid matrix (see the electronic supplementary material).

Since the mathematical formulation in terms of σ seems to be simpler, let us first try to plug the Langmuir kinetics into equation (2.11). From equations (4.1) and (4.2), we can write the partial derivatives appearing in (2.11) as

$$(v_{\text{ads}})_c = k_{\text{ads}} C_0 \sigma^t \left(1 - \frac{k_{\text{ads}} C_0}{k_{\text{ads}} C_0 + k_{\text{des}}} \right), \quad (v_{\text{ads}})_\sigma = -k_{\text{ads}} C_0 (1 - \sigma_\sigma^t), \quad (v_{\text{des}})_\sigma = k_{\text{des}}, \quad (4.3)$$

which are, of course, evaluated at the steady state ($1, k_{\text{ads}} C_0 \sigma^t / (k_{\text{ads}} C_0 + k_{\text{des}})$). Notice that in order to satisfy $(v_{\text{ads}})_\sigma < 0$ we need to have $\sigma_\sigma^t < 1$, which certainly holds for non-cooperative systems, where converting an empty site into an occupied site cannot cause the appearance of an unoccupied site. By using the above expressions and defining $K_{\text{eq}} = k_{\text{ads}}/k_{\text{des}}$, we can rewrite equation (2.11) as

$$\begin{aligned} & \left(1 - \varepsilon \frac{\sigma^t K_{\text{eq}}}{C_0 K_{\text{eq}} + 1} \right) (\ln \phi)_\sigma + \varepsilon \sigma \frac{\sigma^t K_{\text{eq}}}{C_0 K_{\text{eq}} + 1} \frac{1 - \phi}{\phi} \\ & \leq -\frac{\varepsilon}{C_0} \frac{1 - \phi}{\phi} - \frac{1 + C_0 K_{\text{eq}}}{\sigma^t} \left(\frac{1}{C_0 K_{\text{eq}}} + \frac{\delta}{C_0 k_{\text{ads}}} + (1 - \sigma_\sigma^t) \right). \end{aligned} \quad (4.4)$$

The previous expression shows that it is possible in principle to have chemomechanical oscillations even with simple Langmuir kinetics and that, as long as $(1 - \varepsilon(\sigma^t K_{\text{eq}} / (C_0 K_{\text{eq}} + 1))) > 0$, only decreasing porosity functions are able to satisfy this condition. At this point, it would be tempting to substitute equations (3.2)–(3.5) in (4.4) to test which types of porosity functions would satisfy it, but should we adopt this straightforward approach, we would quickly encounter difficulties. The problem is that the porosity that enters (4.4) is evaluated at the steady state, but the steady state value of σ explicitly depends on σ^t , which is in turn expressed as a function of the porosity, leading to self-recursive definitions, which may greatly complicate the mathematical treatment. Since the source of this self-recursiveness is the fact that the steady state value of σ depends on σ^t , we can overcome the problem by switching to the formulation in terms of the fractional coverage θ , whose steady state value according to equations (4.1) and (4.2) is $\theta^0 = K_{\text{eq}} C_0 / (K_{\text{eq}} C_0 + 1)$. The θ framework also offers the advantages of a more intuitive interpretation of the microscopic properties of the solid matrix in relation to its adsorption-induced swelling, and of working with a variable that is normalized between 0 and 1.

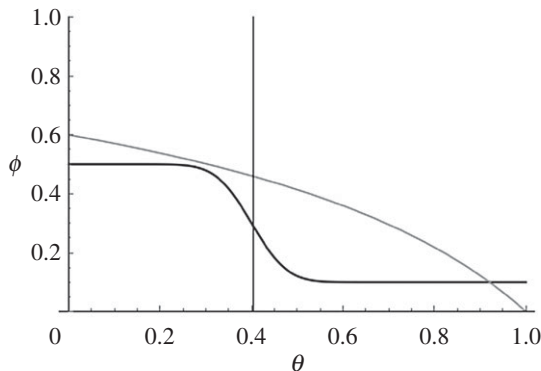


Figure 1. Porosity as a function of θ . The black curve is the porosity function defined by (5.1) with $\phi_M = 0.5$, $\phi_m = 0.1$, $\theta_j = 0.4$ and $\alpha = 11.5$. For reference, we also plot in grey ϕ_{crit} as a parametric curve versus θ^0 when \tilde{K}_{eq} varies from 10^{-3} to 10^3 (with $\gamma = -\frac{1}{3}$ and $\tilde{\rho} = 0.1$). The first condition in (4.12) is satisfied if at $\theta = \theta^0$ the black curve lies below the grey one. The vertical bar marks the location of θ^0 , a case that is analysed in more detail below, corresponding to $\tilde{K}_{eq} = 0.68$.

By substituting equations (4.1) and (4.2) into (3.6) and (3.7) and taking into account equations (3.2), (3.4), (3.14) and (3.15) we can write the evolution equations for our system as

$$\frac{dc}{d\tau} = -\frac{[\tilde{\rho}/\phi + c(\ln\phi)_\theta]}{1 + (\ln\phi)_\theta(1-\gamma)(\phi/(1-\phi))\theta} \left(c(1-\theta) - \frac{\theta}{\tilde{K}_{eq}} \right) + \tilde{\delta}(1-c) \quad (4.5)$$

and

$$\frac{d\theta}{d\tau} = \frac{1}{1 + (\ln\phi)_\theta(1-\gamma)(\phi/(1-\phi))\theta} \left(c(1-\theta) - \frac{\theta}{\tilde{K}_{eq}} \right), \quad (4.6)$$

where we have introduced the non-dimensional quantities

$$\tau = C_0 k_{ads} t, \quad \tilde{\rho} = \frac{n_s}{C_0 V_{bM}}, \quad \tilde{K}_{eq} = C_0 K_{eq}, \quad \tilde{\delta} = \frac{\delta}{C_0 k_{ads}}. \quad (4.7)$$

Thanks to the non-dimensionalization (4.7) we are able to characterize the system in terms of just three independent dimensionless parameters: \tilde{K}_{eq} , $\tilde{\delta}$ and $\tilde{\rho}$. The parameter \tilde{K}_{eq} represents a normalized equilibrium constant, which controls the equilibrium position θ^0 . The parameter $\tilde{\delta}$ is the ratio between the rate of exchange with the external reservoir and the intrinsic time scale of the reaction, $C_0 k_{ads}$. The parameter $\tilde{\rho}$ represents the ratio between the total volume concentration of sites and the reference gas concentration C_0 . This quantity plays a very important role in our theory, because it controls the importance of the structural changes on the overall dynamics. Notice that $\tilde{\rho}$ is independent of the system-dependent geometric quantities ε_0 and γ . More generally, the independence of equations (4.5) and (4.6) from ε_0 is significant, because it means that these equations are valid regardless of the specific geometric details of the microscopic structure.

The oscillatory instability arises from the term proportional to $(\ln\phi)_\theta$ within the square brackets in equation (4.5), which, as we already saw, must be negative. Notice, however, that the effect of this destabilizing structural term is opposed by the term proportional to $\tilde{\rho}$, which is always positive. If $\tilde{\rho}$ is large, the quantity within square brackets in (4.5) will be less dependent on changes in porosity, and the steady state will be stable. This result suggests that the emergence of oscillations will be facilitated in systems where there are more gas molecules relative to the number of adsorption sites.

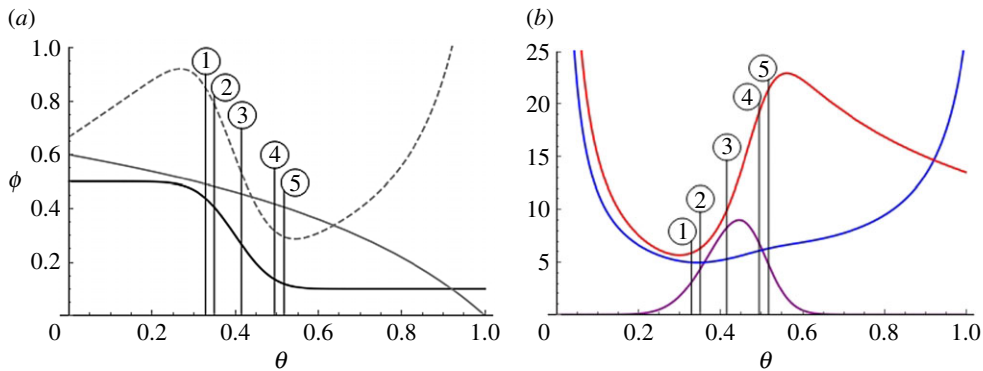


Figure 2. Porosity function (a) and bifurcation diagram (b) for $\phi_M = 0.5$, $\phi_m = 0.1$, $\theta_j = 0.4$, $\alpha = 10$, $\tilde{\rho} = 0.1$, $\tilde{\delta} = 1$ and $\gamma = -\frac{1}{3}$. The solid black and grey curves represent the same quantities as in figure 1. The dashed grey curve marks the value of the term within square brackets in (4.10). The blue, red and purple curves, respectively, are ℓ_{\min} , ℓ_{\max} and $(\ln \phi)_\theta$: the steady state is unstable when the purple curve lies between the blue and red curves. The grey, red and blue curves have been plotted as parametric curves versus θ^0 when \tilde{K}_{eq} varies from 10^{-3} to 10^3 . The labelled vertical bars mark the positions of five different values $\{\textcircled{1}, \textcircled{2}, \textcircled{3}, \textcircled{4}, \textcircled{5}\}$ of θ^0 corresponding to $\tilde{K}_{\text{eq}} = \{0.490, 0.538, 0.708, 0.977, 1.072\}$.

Switching to more quantitative terms, from equations (4.1) and (4.2) (and taking again into account equations (3.2), (3.4), (3.14) and (3.15)), we can calculate that for Langmuir kinetics

$$(v_{\text{ads}})_\theta = -\frac{V^{-\gamma} C_0^2 k_{\text{ads}}}{\varepsilon_0} \tilde{\rho} (1 - \phi)^{-(1+\gamma)} \left(1 - (\ln \phi)_\theta (1 - \gamma) \frac{\phi}{1 - \phi} (1 - \theta^0) \right) \quad (4.8)$$

and

$$(v_{\text{des}})_\theta = \frac{V^{-\gamma} C_0^2 k_{\text{ads}}}{\varepsilon_0} \frac{\tilde{\rho}}{\tilde{K}_{\text{eq}}} (1 - \phi)^{-(1+\gamma)} \left(1 + (\ln \phi)_\theta (1 - \gamma) \frac{\phi}{1 - \phi} \theta^0 \right), \quad (4.9)$$

which are guaranteed to be in agreement with (3.11) under our working hypothesis $(\ln \phi)_\theta < 0$. Substituting the above equations into the conditions for the Hopf bifurcation (3.16) and (3.17) and rearranging in terms of $(\ln \phi)_\theta$ leads to the two inequalities

$$-(\ln \phi)_\theta \geq \ell_{\min} = \frac{1}{(1 + \gamma)} \frac{1 - \phi}{\phi} \frac{1 + \tilde{K}_{\text{eq}}}{\tilde{K}_{\text{eq}}} \left[\frac{(1/\tilde{\delta})(1 + 1/\tilde{K}_{\text{eq}} + (1/(1 + \tilde{K}_{\text{eq}}))(\tilde{\rho}/\phi)) + 1}{(1/\tilde{\delta})(1/(1 + \gamma)\tilde{K}_{\text{eq}})((1 - \phi)/\phi) + 1} \right] \quad (4.10)$$

and

$$-(\ln \phi)_\theta < \ell_{\max} = \frac{1}{(1 + \gamma)} \frac{1 - \phi}{\phi} \frac{1 + \tilde{K}_{\text{eq}}}{\tilde{K}_{\text{eq}}}. \quad (4.11)$$

A necessary but not sufficient requirement in order to have oscillations is thus to identify a region of the parameter space for which $\ell_{\min} < \ell_{\max}$. This is possible if and only if the term within square brackets in (4.10) is smaller than 1, which—assuming $(1 + \gamma) > 0$ —translates into

$$\phi < \phi_{\text{crit}} = \frac{1 - (1 + \gamma)(\tilde{K}_{\text{eq}}/(1 + \tilde{K}_{\text{eq}}))\tilde{\rho}}{1 + (1 + \gamma)(1 + \tilde{K}_{\text{eq}})}, \quad \text{with } 0 < (1 + \gamma) \frac{\tilde{K}_{\text{eq}}}{1 + \tilde{K}_{\text{eq}}} \tilde{\rho} < 1. \quad (4.12)$$

Thus, in addition to the negative slope rule we discussed earlier, oscillations with Langmuir kinetics require that the value of the porosity at the steady state does not exceed a threshold value ϕ_{crit} determined by \tilde{K}_{eq} and $\tilde{\rho}$, which in turn must also respect the second condition in (4.12). For $\gamma = -\frac{1}{3}$, this latter condition becomes $0 < \theta_0 < 3/2\tilde{\rho}$, which is automatically (although not exclusively) satisfied if we keep $\tilde{\rho} < \frac{3}{2}$. It therefore seems that oscillations are more likely to occur if $\tilde{\rho}$ is not too large. On a similar note, we observe that the spread between ℓ_{\min} and ℓ_{\max} increases when the term within square brackets in (4.10) becomes smaller. If $\tilde{\delta}$ is very large, this

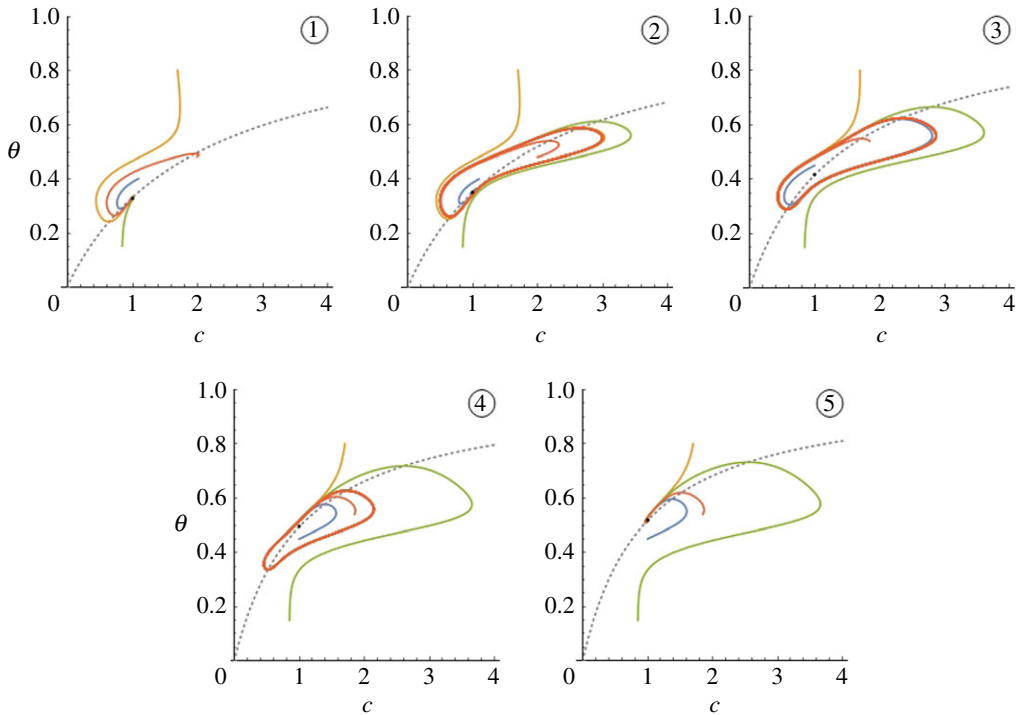


Figure 3. Numerically calculated phase portraits for the five sets of parameters described in figure 2. The four curves in each panel correspond to four different initial conditions. The black point marks the location of the steady state. The dotted grey curve is the nullcline $d\theta/d\tau = 0$. The numerical integrations in this and the following figures have been performed with a Runge–Kutta algorithm, by using the NDSolve function of Mathematica.

quantity approaches 1, making oscillations impossible. Thus, oscillations are more easily obtained for small values of both $\bar{\rho}$ and $\bar{\delta}$.

Once all the above conditions are met, the ability of the system to produce chemomechanical oscillations will only depend on the structural response of the solid matrix with respect to the concentration of adsorbate. In our theory, this response is expressed in terms of the functional dependence of ϕ on θ . If we use a simple linearly decreasing porosity of the form

$$\phi(\theta) = \phi_M - (\phi_M - \phi_m)\theta, \quad (4.13)$$

it is possible to prove that equations (4.10) and (4.11) are never satisfied. This means that, in order to generate sustained oscillations with a simple Langmuir scheme, one needs a nonlinear dependence of the porosity on the fractional coverage.

5. Numerical results

In order to gain more intuition into the role played by the control parameters on the emergence of oscillations, we perform numerical integrations of equations (4.5) and (4.6) by introducing the sigmoidal porosity function

$$\phi(\theta) = \phi_m + (\phi_M - \phi_m)\left(\frac{1}{2} + \frac{1}{2} \operatorname{Erf}[-\alpha(\theta - \theta_j)]\right), \quad (5.1)$$

which smoothly decreases from an upper plateau ϕ_M to a lower value ϕ_m in the neighbourhood of $\theta = \theta_j$; the sharpness of the jump is controlled by the parameter α (figure 1).

Examining figures 2–4, we observe that the instability region is bounded by a supercritical Hopf bifurcation for large values of θ^0 (between ⑤ and ④), which gives rise to a stable limit cycle,

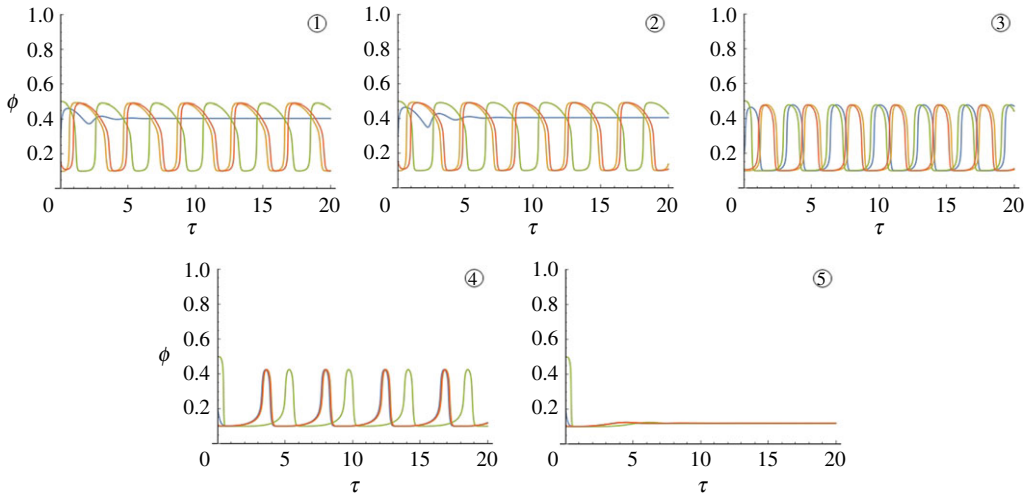


Figure 4. Numerically calculated time evolution of the porosity calculated from equation (5.1) for the five cases in figure 3. The four differently coloured curves in each panel refer to the trajectories of the same colour in figure 3.

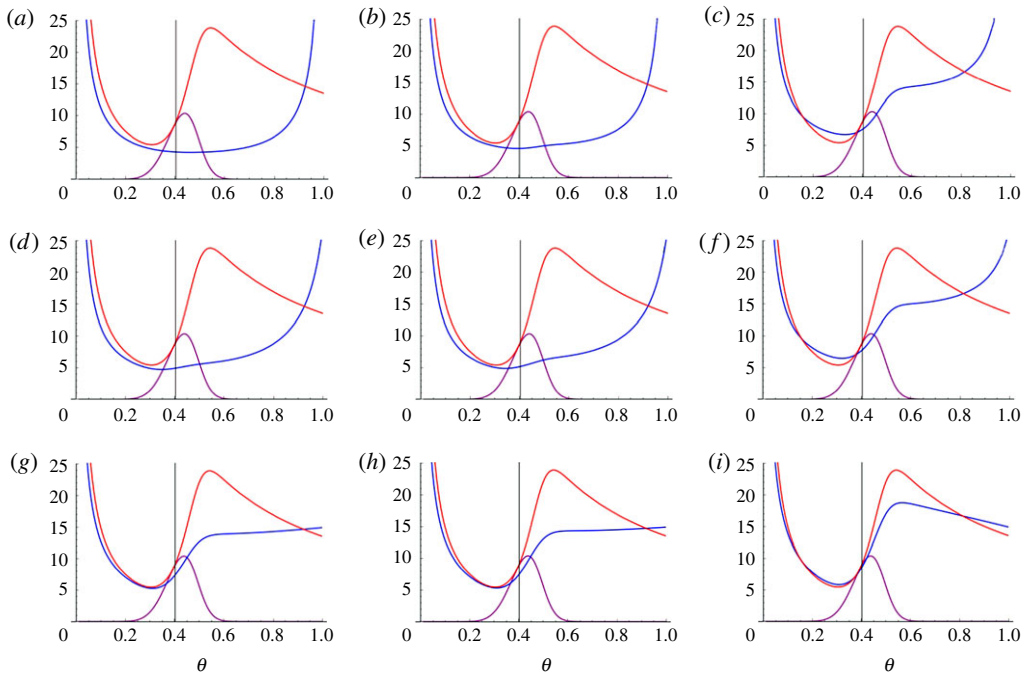


Figure 5. Bifurcation diagrams for the porosity function and equilibrium constant described in figure 1 at several values of $\tilde{\rho}$ and $\tilde{\delta}$. (*a,d,g*), (*b,e,h*) and (*c,f,i*) columns of plots, respectively, have $\tilde{\rho} = \{0.01, 0.1, 1\}$. (*a-c*), (*d-f*), (*g-i*) rows of plots, respectively, have $\tilde{\delta} = \{0.1, 1, 10\}$. Colour coding is the same as in figure 2*b*. The vertical bar marks the position of θ^0 .

and by a subcritical Hopf bifurcation for small values of θ^0 (between ③ and ②), which produces an unstable limit cycle within the previous stable one. The limit cycle formed by the supercritical Hopf bifurcation survives past the subcritical Hopf bifurcation and disappears through a saddle–node bifurcation of limit cycles (between ② and ①) after colliding with the unstable limit cycle.

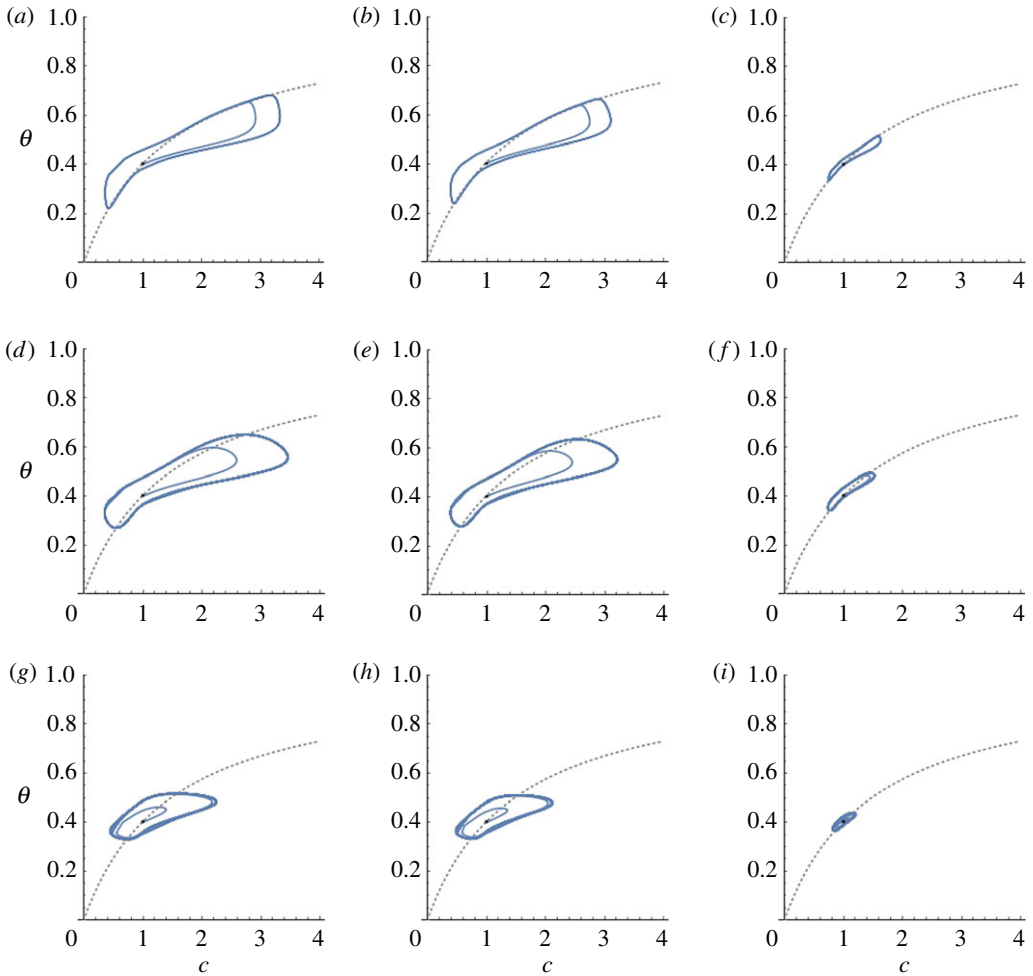


Figure 6. Numerically calculated phase portraits for the nine sets of parameter values in figure 5. Colour coding is the same as in figure 3. The initial condition of the only plotted trajectory in each panel was chosen to be very close to the (unstable) steady state.

Therefore, if we keep $\tilde{\rho}$ and $\tilde{\delta}$ constant, oscillations can emerge in essentially two ways as we change the value of \tilde{K}_{eq} : either gradually and with small initial amplitude—when decreasing \tilde{K}_{eq} from the high θ^0 stability region—or abruptly with large initial amplitude—when increasing \tilde{K}_{eq} from the low θ^0 stability region.

Finally, figures 5–7 exhibit the effect of varying $\tilde{\rho}$ and $\tilde{\delta}$ while keeping \tilde{K}_{eq} constant. Figure 5 demonstrates that the region where oscillations are possible (i.e. the region between the red and blue curves) shrinks as we move to larger values of either $\tilde{\rho}$ (moving from (a,d,g) to (c,f,i)) or $\tilde{\delta}$ (moving from $(a-c)$ to $(g-i)$), as we had already predicted by looking at the form of the term within square brackets in (4.10). The numerical simulations provide insights not available from a linear stability analysis: how $\tilde{\rho}$ and $\tilde{\delta}$ affect the amplitude and the period of oscillations. Figure 6 shows that increasing either $\tilde{\rho}$ or $\tilde{\delta}$ tends to decrease the amplitude of the limit cycle, with $\tilde{\rho}$ having a larger effect than $\tilde{\delta}$. This is confirmed by looking at figure 7, which shows the time evolution of ϕ and θ . These time series also show that increasing $\tilde{\delta}$ causes a dramatic decrease in the period of oscillations, while increasing $\tilde{\rho}$ has a more modest (and non-monotonic) effect on the period. In other words, the numerical integrations suggest that the amplitude of oscillation is primarily controlled by $\tilde{\rho}$ while the period depends more strongly on $\tilde{\delta}$.

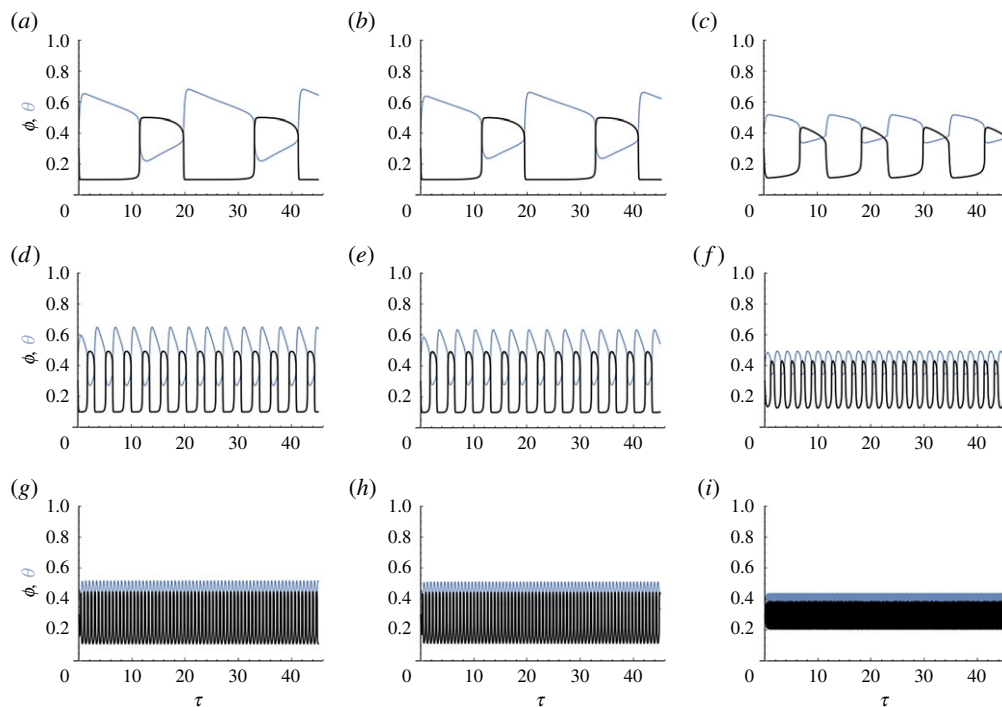


Figure 7. Numerically calculated time evolution of ϕ (black curve) and θ (light blue curve) for the nine plots in figure 6.

6. Conclusion

The aim of this work has been to present a proof of concept for a new class of chemomechanical oscillators that do not rely on an intrinsically oscillating reaction. Our primary goal was to show that, when structural changes are coupled with simple adsorption/desorption kinetics, they can provide a dynamical feedback that leads to the emergence of non-trivial behaviours. We have shown that, in order for such behaviours to arise, the structural changes must fulfil several requirements. One general criterion is that the porosity of the system must decrease as the surface coverage of adsorbate increases near the steady state, i.e. there is an adsorption-induced swelling of the solid matrix around the steady state.

In the particular case of Langmuir kinetics, we mentioned that a linear dependence of the porosity on the adsorbate loading cannot create an instability. This result suggests that, in order to compensate for the relative simplicity of the reaction, we need to introduce a nonlinear feedback in the dynamical response of the structure. An interesting thing to test in the future is whether this constraint may be relaxed if nonlinear adsorption/desorption kinetics (involving, for example, different degrees of molecular cooperativity) are taken into account or, in other words, what are the minimal requirements on the adsorption kinetics in order to build oscillations with a linear porosity function. The introduction of one or more competing adsorbates or of chemical reactions on the surface are additional features that would make the model more generally applicable (and more prone to oscillation).

We also showed that there may be additional universal restrictions—in addition to the general decreasing slope of the porosity function—in order to build oscillations with a given adsorption scheme. In the case of the Langmuir scheme, we found that the value of the porosity at the steady state must not exceed a critical threshold that depends on the parameters of the system. Finally, we found in a simple numerical example that oscillations are possible within a relatively large range of values of the control parameters and can arise with a wide range of amplitudes and periods.

Although we recognize that at this stage our results are only a theoretical prediction, we hope that this work may inspire future investigations aimed at experimentally finding, or even designing, examples of ‘poroscillators’. A critical problem to solve toward that end is to identify the microscopic properties that a material must have in order to produce the kind of nonlinear response needed for oscillations. Finally, an important question that we do not address in this paper concerns the thermodynamic properties of the class of systems discussed here. While standard chemical oscillators are kept out of equilibrium by constant introduction of fresh reactants and removal of products, the present system does not have a net reaction flux from reactants to products. In other words, the oscillations seem to occur around a chemical equilibrium state, despite the very well-known thermodynamic truth that chemical oscillations cannot occur around equilibrium if mechanical equilibrium is also established in the system [11]. This apparent contradiction may be resolved by considering that the system studied here is never in a state of mechanical equilibrium, owing to its continuous expansion and contraction cycles. This observation suggests that these oscillations may be a particular case of mechanical oscillations that are established and maintained *through* the action of a chemical reaction, rather than being ‘fuelled’ by the chemistry itself. In other words, the poroscillator seems to be akin to a metronome whose internal cogs and wheels are represented by the chemical reaction, but where the spring that keeps the system far from equilibrium is driven by something else. It would therefore be very interesting to examine more closely the thermodynamics of the poroscillator to try to identify the thermodynamic driving force responsible for keeping the system out of balance, thereby providing the conditions needed for oscillations.

Data accessibility. This article has no additional data.

Competing interests. We declare we have no competing interests.

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