Marangoni Based Motile Oil-Droplets in Simulated Artificial Chemistry

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Empirical work has characterized *motile oil-droplets*—small, self-propelled oil-droplets whose active surface-chemistry propels them through their environment. Certain motile-oil droplets (MOD) move toward environments that accelerate or enable their motion-producing reactions, suggesting the possibility that they are minimal examples of *autonomous agents*—construed as precarious self-maintaining systems that act to satisfy their own needs (Hanczyc and Ikegami, 2010; Barandiaran et al., 2009; Barandiaran and Egbert, 2013).

We have developed a new computational model of MOD, where a droplet is modelled as a disc that moves through a 2D spatial environment containing diffusing chemicals. The concentration of reactants on its surface change by way of chemical reactions, diffusion, Marangoni flow (the equilibriation of surface tension), and exchange with the droplet's local environment. Droplet motility is a biproduct of Marangoni flow, similar to the motion-producing mechanism observed in the lab (Hanczyc, 2014). The model is designed to facilitate customization and can be easily reconfigured to explore diverse chemicals and chemical reaction networks operating on the surface of the simulated oil-droplets situated within customizable environmental conditions.

Model

The model simulates a 2D space that contains a MOD and its environment of diffusing chemicals.

Environment. The simulated environment is a circular 'petri dish,' 10mm in radius which contains diffusing 'environmental chemicals.' The concentration of each environmental chemical, $v \in \mathbf{v}$, is a function of position in a 2D space ($\mathbf{p} \in \mathbb{R}^2$) and time ($t \in \mathbb{R}$), which changes by way of chemical diffusion and exchange with the surface of the MOD according to:

$$\frac{dv(\mathbf{p}, t)}{dt} = D_v \nabla^2 v - x(\mathbf{s}, \mathbf{v}, \theta, \mathbf{q}) \qquad (1)$$

where D_v is the diffusion constant of v and $x(\mathbf{s}, \mathbf{v}, \theta, \mathbf{q})$ is a function that describes the exchange between the MOD surface and the environment (defined below).

Motile Oil Droplet. The MOD is modelled as a disc of fixed radius r=1mm. Its centre, $\mathbf{q} \in \mathbb{R}^2$, is constrained such that the entire MOD always lies within the petri dish. We simulate the dynamics of its surface chemistry, which involves one or more 'surface chemicals' or 'reactants.' The concentration of each reactant $s \in \mathbf{s}$ is a function of its position on the surface of the MOD, $\theta \in (0, 2\pi)$ and time, $t \in \mathbb{R}$. Its rate of change is the sum of four processes,

$$\frac{d\mathbf{s}(\theta, t)}{dt} = r(\mathbf{s}) + f(\mathbf{s}) + m(\mathbf{s}) + x(\mathbf{s}, \mathbf{v}, \theta, \mathbf{q}) \qquad (2)$$

which we now describe.

Chemical Reactions. $r(\mathbf{s})$ describes the change in surface reactants caused by chemical reactions. These reactions are specified as mass action kinetic equations, which are automatically translated into the $r(\mathbf{s})$ term.

Peripheral Diffusion. $f(\mathbf{s})$ describes the diffusion of $\mathbf{s}$ around the surface of the MOD. The diffusive flux in the concentration of each species, $F_\mathbf{s} = -K_s \frac{\partial s}{\partial \theta}$, which leads to the classic 1D diffusion equation, that we can use to calculate the change in s over time: $f(\mathbf{s}) = K_s \frac{\partial^2 s}{\partial \theta}$. Here K_s is the diffusion rate constant for the species and $s = f(\theta)$ is a function, representing the concentration of that species around the perimeter of the droplet.

Marangoni Flow. Each species is associated with a surface tension constant, γ_s. The interfacial tension, Γ, varies locally over the surface of the droplet, and is calculated as the sum of the local concentration of the species, each scaled by its surface tension constant. $\Gamma = \sum_{\forall s} \gamma_s s$. Asymmetry in Γ is resolved by a flux of all reactants, G, proportional to the Γ-gradient : $G = -K_\Gamma \frac{\partial \Gamma}{\partial \theta}$. The change in s due to the Marangoni flow is thus: $m(\mathbf{s}) = K_\Gamma \frac{\partial \Gamma}{\partial \theta} s$. Conceptually, this equation states that the concentration of each reactant changes at a rate proportional to its local concentration s and the velocity of the Marangoni induced flux. It is similar to diffusion, but the gradient being resolved is that of total surface tension, not the concentration of the species. So, unlike diffusion, if this process were the only one operating, it could maintain an asymmetrical distribution of chemicals (given asymmetrical initial conditions).
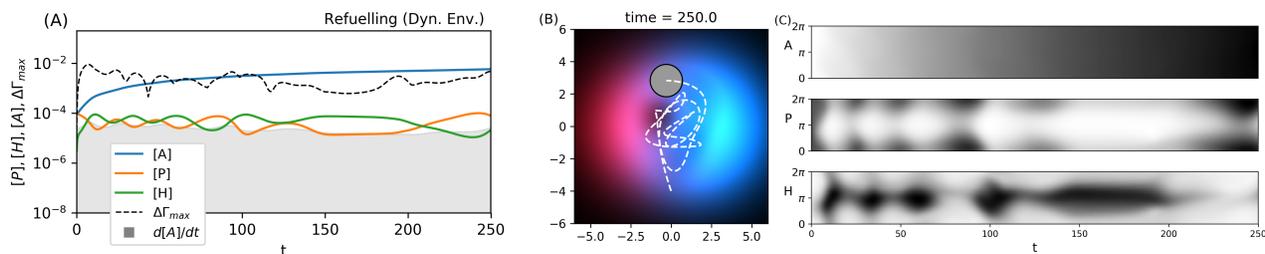
Figure 1: Experimenting with two, spatially separated metabolic resources. (A) time-series show the average concentration of each surface-reactant and the maximum difference in surface tension between any two points on the MOD's surface (dashed line). and the rate of A-production (gray shaded area). (B) the final state of the environment and MOD trajectory and final position. (C) the normalized concentration of each chemical varies over the surface of the droplets (vertical axis) over time (horizontal axis).

Environment/Surface Exchange. $x(\mathbf{s}, \mathbf{v}, \theta, \mathbf{q})$ describes the exchange of reactants between the MOD surface and the environment. This exchange approaches an equilibrium which is defined by the parameter $H_v \in \mathbf{H}$ that describes the tendency of chemical v to enter or exit the MOD interface, and a rate parameter, $\chi_v \in \boldsymbol{\chi}$, thus:

$$x(\mathbf{s}, \mathbf{v}, \theta, \mathbf{q}) = \boldsymbol{\chi}\left(\mathbf{Hs} - (1 - \mathbf{H})V(\mathbf{q}, \theta)\right) \quad (3)$$

in this equation, $V(\mathbf{q}, \theta) = f(\mathbf{q}, \theta) * \mathbf{v}$ is a regional sampling of the environmental chemicals, expressed by a discrete convolution of the environmental concentrations, $\mathbf{v}$ with a sampling kernel, $f(\mathbf{p})$, which corresponds to a segment of the MOD disc.

Droplet Motion Marangoni flow induces a tangential flow in the surrounding medium, resulting in an acceleration to the droplet in the opposite direction. We assume viscosity to be high and model velocity as proportional to this acceleration, thus:

$$\frac{d\mathbf{q}}{dt} = k_v \int G(\theta)(\theta + \pi/2) \, d\theta \quad (4)$$

where $k_v = 2.5 \times 10^4$ is a constant that scales the amount of motion produced by the Marangoni flux.

Results

Our first explorations of this model recreate the results of empirical MOD work presented in (Hanczyc et al., 2007), where a nitrobenzene oil-droplet containing containing oleic anhydride was placed in an alkaline aqueous environment with a surfactant that facilitates the formation of droplets. The oleic anhydride at the surface of the droplet hydrolizes into two amphiphilic molecules that change the local surface tension. The surface flows to equilibriate any asymmetry in the surface tension and when this Marangoni flow is coherent, the flow at the surface induces a flow in the local aqueous environment via fluid friction, propelling the droplet through the aqueous medium. The rate of hydrolysis increases with alkalinity, and Marangoni flow is such that the reaction drives the droplet toward local environmental conditions that accelerate that reaction. This is an interesting example of what has been called metabolism-based behaviour—a precarious dissipative structure which regulates its environment in response to its own metabolic health (Egbert et al., 2010; Egbert and Pérez-Mercader, 2016) which has been considered a basic form of cognition or agency (Bich et al., 2016; Egbert et al., 2009; Ruiz-Mirazo et al., 2017; Froese et al., 2013; Virgo, 2011).

To model this, we simulate three reactants: A, an amphiphilic molecule that increases surface tension; H, which is a proxy for alkalinity; and P, a oleic-anhydride-like 'precursor' molecule that is transformed into $2A$ when H is present according to the following reaction $P + H \rightarrow 2A$, with a reaction rate $\phi = 1 \times 10^4$.

The MOD is seeded with $A_0 = P_0 = 10^{-4}$, $H_0 = 0$ and placed in an environment with a 2D Gaussian gradient of H. The simulated MOD performs as expected, and moves up the gradient toward the conditions that are conducive to its 'metabolic' reaction. We have also recapitulated some of the work conducted in (Matsuno et al., 2007) confirming that the motion of the droplet accelerates the metabolic reaction.

Taking advantage of the easy reconfigurability of the model, we have conducted additional experiments looking at a MOD which can replenish its precursor from its environment (Fig. 1). In this condition, with spatially separated resources (P and H), the MOD moves back and forth between the two, the motion that is necessary to maintain the continued operation of the metabolic reaction. Work is ongoing to examine this kind of metabolism-based behaviour.

Future work

The model is easily reconfigured to simulate different artificial chemistry reaction networks, and thus provides a platform for investigating how Marangoni-based motility might be made employed in behaviours more sophisticated than basic chemotaxis, for instance to include adaptation, memory or learning. Such advances in simulation may suggest directions for future laboratory-based efforts to create increasingly impressive MOD technology and to understand the role that metabolism-based behaviour may have played in facilitating the earliest stages of evolution (Egbert et al., 2011; Egbert and Pérez-Mercader, 2016).

Acknowledgements

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