Problem sheet on "Chemically Active Droplets"

1 Concrete problem: Isolated droplets

This problem focuses on analytic calculations of isolated spherical droplets.

1.1 Stationary diffusive flux outside a passive droplet

Consider a spherical 3D droplet of radius R in a large dilute phase. The concentration field $c(\boldsymbol{r})$ of the droplet material is governed by a simple diffusion equation, $\partial_t c = D\nabla^2 c$, with diffusivity D. Solve for the stationary diffusion profile outside the droplet, assuming that c is fixed to $c_{\text{out}}^{\text{eq}}$ by the phase equilibrium at the droplet interface, and approaches c_∞ far away. Use the result to calculate the local flux $\boldsymbol{j}$ according to Fick's first law, $\boldsymbol{j} = -D\nabla c$, and determine the integrated flux J_{out} away from the droplet interface.

1.2 Stationary diffusive flux outside a active droplet

Repeat the calculations from section 1.1 assuming that the droplet material in the dilute phase is now described by the reaction-diffusion equation

$$\partial_t c = D\nabla^2 c + k(c_0 - c) \,, \tag{1.1}$$

where k is the reaction rate and c_0 governs the reaction equilibrium. Calculate the integrated flux J_{out} using the same assumptions as before. When are reactions relevant?

1.3 Stationary states of active droplet

The growth rate of an active droplet of volume V is described by

$$\partial_t V \approx \frac{J_{\text{in}} - J_{\text{out}}}{\Delta c} \,, \tag{1.2}$$

where Δc approximates the concentration difference between the two phases. In the simplest case, the flux inside the droplet is $J_{\text{in}} \approx \Gamma_{\text{in}} V$ with a constant Γ_{in}, whereas $J_{\text{out}} \approx 4\pi R D_{\text{out}}\big(c_{\text{out}}^{\text{eq}} - c_\infty\big)$ with the concentration far away controlled by reactions, $c_\infty = c_{\text{out}}^{(0)} + \Gamma_{\text{out}}/k_{\text{out}}$. Here, R is the droplet radius (so that $V = \frac{4}{3}\pi R^3$), D is the diffusivity, $c_{\text{out}}^{\text{eq}} = c_{\text{out}}^{(0)}(1+\ell/R)$ with positive constants $c_{\text{out}}^{(0)}$ and ℓ, and c_∞ is the constant concentration far away from the droplet. What equation governs the stationary state radius of droplets? Solve the equation in the limit of small ($R \ll \ell$) and large ($R \gg \ell$) droplet radii R. Bonus task: Determine the correction of order ℓ in the latter case!

1.4 Stability of active droplet

Reconsider the stationary solutions obtained in section 1.3 and determine their stability (with respect to small perturbations of the droplet radius). Interpret the results for internally-maintained droplets ($\Gamma_{\text{in}} > 0$, $c_\infty < c_{\text{out}}^{(0)}$) and externally-maintained droplets ($\Gamma_{\text{in}} < 0$, $c_\infty > c_{\text{out}}^{(0)}$).

2 Open-ended problem: Simulation of active droplets

This problem focuses on numerical simulations of active droplets. The aim is to simulate the extended Cahn-Hilliard equation for the volume fraction field ϕ,

$$\partial_t \phi = \nabla^2 (f'(\phi) - \nabla^2 \phi) + s(\phi) \,, \tag{2.1}$$

where we for simplicity choose the free energy density as $f(\phi) = \frac{1}{2}\phi^2(1-\phi)^2$, implying $f'(\phi) = \phi(\phi-1)(2\phi-1)$, and the reaction rate as $s(\phi) = k(\phi - \phi_0)$. The equations have already been non-dimensionalized for convenience. The partial differential equation (2.1) needs to be augmented by boundary conditions, and we focus on periodic conditions for simplicity.

You can simulate this equation with any method that you are familiar with, but the associated jupyter notebook provides a simple implementation that solves this equation based on the Python package `py-pde`, which we develop [2]. After getting acquainted with the code, there are numerous ideas for how to extend this simulation:

1. Visualize the final state of passive and active droplets. What hallmarks of non-equilibrium systems can you identify?
2. Visualize the kinetics starting from different initial conditions. Can you identify the spinodal length scale λ_{spin} given by Eq. (2.10) in the lecture notes?
3. Quantify the radius of active droplets. How does it compare to expectations?
4. Identify crucial control parameters of the droplet radius.
5. How can you influence the position of droplets?
6. Can you generate interesting temporal dynamics, e.g., using external driving?
7. How can you control when droplets form and when they dissolve again?

References

[1] Noah Ziethen and David Zwicker. Heterogeneous nucleation and growth of sessile chemically active droplets. *J. Chem. Phys.*, 160(22):224901, 06 2024. ISSN 0021-9606. doi: 10.1063/5.0207761. URL `https://doi.org/10.1063/5.0207761`.

[2] David Zwicker. py-pde: A python package for solving partial differential equations. *J. Open Source Softw.*, 5(48):2158, 2020. doi: 10.21105/joss.02158. URL `https://doi.org/10.21105/joss.02158`.