Non-equilibrium phase separation with chemical reactions

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Canonical model

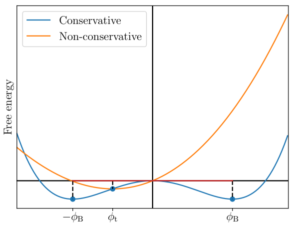
A class of systems with conservative phase separation mechanisms as well as chemical reactions. Examples include

- Self-propelled bacteria with birth-death dynamics [1,2]
- Biomolecular condensates [3]
- Chemically active bi-polymer blends [4]

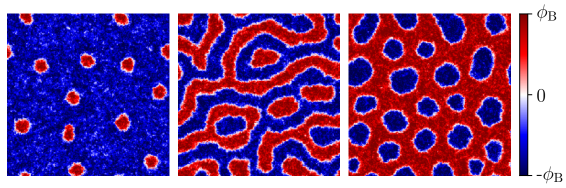
Canonical model: Model B and Model A with different chemical potentials. Scalar field ϕ: rescaled density or composition variable.

$$\partial_t \phi = M_1 \nabla^2 \mu_1 - M_2 \mu_2 + \Lambda$$
$$\mu_1 = -\alpha\phi + \beta\phi^3 - \kappa \nabla^2 \phi$$
$$\mu_2 = u(\phi - \phi_a)(\phi - \phi_t)$$
$$\langle \Lambda(\boldsymbol{x}, t)\Lambda(\boldsymbol{y}, s)\rangle = 2\epsilon\left[-M_1 \nabla_x \nabla_y + M_2\right]\delta^3(\boldsymbol{x} - \boldsymbol{y})\delta(t - s)$$

Conservative dynamics: Double-well free energy with two stable binodals
Non-conservative dynamics: Cubic free energy with one stable fixed point at target density ϕ_t
Absorbing state at $\phi = \phi_a$ but far away



Steady state solution: arrested phase separation



Linear stability analysis

Expand $\phi(\boldsymbol{x}) = \phi_t + \int \frac{d^3q}{(2\pi)^3} \delta\phi(\boldsymbol{q}) e^{-i\boldsymbol{q}\cdot\boldsymbol{x}}$,

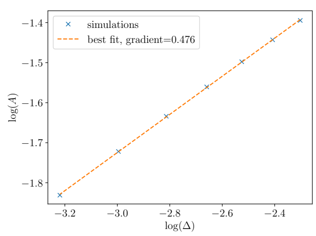
$$\partial_t \phi_q = \left[\left(\frac{\tilde{\alpha}^2}{4\kappa} - u\right) - \kappa(q^2 - q_c^2)^2\right]\phi_q$$

where $\tilde{\alpha} = \alpha - 3\beta\phi_t^2$, and $q_c = \sqrt{\tilde{\alpha}/2\kappa}$.
$\rightarrow$ Uniform state unstable for $\tilde{\alpha} > \sqrt{4u\kappa}$.

Close to the pattern formation threshold

Let $\Delta = \tilde{\alpha}^2(4\kappa u)^{-1} - 1$.
For small Δ, growth of the most unstable mode q_c saturated by the non-linear terms.

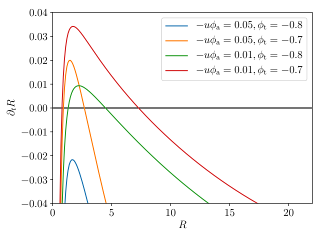
$$\phi(x) \sim \Delta^{1/2}\cos(q_c x)$$



Arrested Ostwald ripening of droplets

Balance flux across the boundary of a droplet in a bath to obtain growth rate of the radius

- Unstable fixed point: the usual Ostwald ripening radius - smaller droplets shrink
- Stable fixed point: stable radius of a droplet



Limit cycle solution

When reaction is slow compared to diffusion,

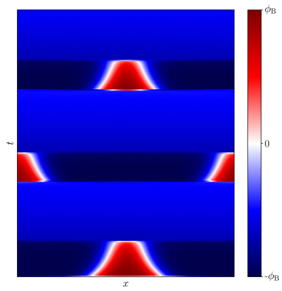


Figure: Space-time plot of a limit cycle where a dense droplet appears and disappears over time.

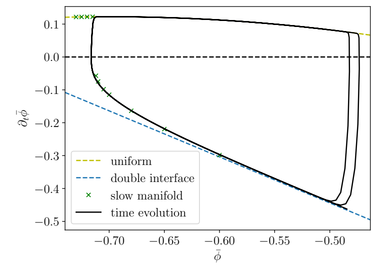


Figure: The same limit cycle projected onto $(\partial_t\bar{\phi}, \bar{\phi})$ where $\bar{\phi}(t) = \int dx \phi(x,t)$. The slow manifold is the steady state solution of the conservative part of the dynamics given $\bar{\phi}$.

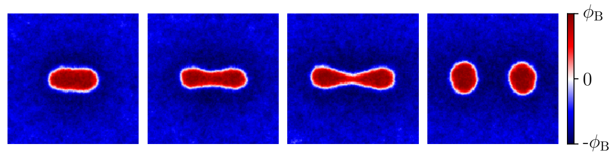
Conditions for the cycles to occur

- Droplet state: enough decrease in the droplet to offset the production in the dilute region, i.e. effective target density close to the binodal
- Uniform state: ϕ_t within the spinodals so the uniform state becomes unstable before ϕ_t is reached.

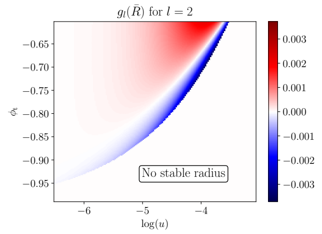
Hysteresis structure essential for limit cycles to occur

Droplet splitting

Spherical droplets are sometimes unstable against shape perturbations



- Ostwald ripening type calculation for perturbations around a spherical droplet
$$R(\theta) = \bar{R} + \sum_l \delta R_l \cos(l\theta)$$
- Linear stability analysis gives $\partial_t \delta R_l = g_l\left(\bar{R}\right)\delta R_l$



Conclusions and perspectives

Conclusions

- We constructed a canonical model for conservative phase separation and chemical reactions.
- The canonical model captures the phenomenologies of the more complicated models [1-4], including limit cycles, arrested phase separation and droplet splitting.

Perspectives

- The limit cycle solution clearly breaks the time reversal symmetry, but it is hard to tell what is non-equilibrium about the steady state patterns $\rightarrow$ need to look at fluctuations

References

[1] Cates ME et al. 2010, PNAS, 107(26).
[2] Grafke T et al. 2017, PRL, 119(18).
[3] Weber C et al. 2019, Reports on Progress in Physics, 82(6).
[4] Glotzer SC et al. 1995, PRL, 74(11).