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LUDWIG-MAXIMILIANS-UNIVERSITÄT MÜNCHEN
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Self-organization and pattern formation
Sheet 4

Exercise 12 – Cahn-Hilliard equation with an additional reaction term

In the lecture you studied a binary mixture in which each individual species is preserved. Now we want to introduce a chemical reaction into the system such that the total number of particles is preserved, but the individual species are not. The simplest reaction to consider is the transformation between species. i.e,

$$A \rightleftharpoons B. \tag{1}$$

In this situation, the dynamics of local concentration of the A-particle is governed by the Cahn-Hilliard equation, modified by an additional reaction term

$$\partial_t c = \Gamma \nabla^2 \mu(c) - \Lambda \mu(c), \tag{2}$$

where Λ and Γ are positive Onsager coefficients. *(Note: This model is like adding model A and model B together.)* The chemical potential given by $\mu(c) = \delta \mathcal{F}[c] / \delta c$. $\mathcal{F}[c]$ is the Ginzburg-Landau free energy functional for a binary mixture

$$\mathcal{F}[c] = \int_{\mathbb{R}^d} d^d x \left[f(c) + \frac{\kappa}{2} (\nabla c)^2 \right], \tag{3}$$

with $f(c) = -\frac{r}{2}(c-c_c)^2 + \frac{u}{4}(c-c_c)^4$ and c_c is a positive constant (the critical concentration).

a) To simplify the equations we consider density deviations ϕ from the critical density $\phi = \nu(c - c_c)$, where ν is the molecular volume. By rescaling $\phi = \alpha \phi'$, show that the eq.(2) can be rewritten as

$$\partial_t \phi' = \left(\Gamma' \nabla^2 - \Lambda' \right) \left(-\phi' + \phi'^3 - \kappa' \nabla^2 \phi' \right). \tag{4}$$

What assumption is made in this rescaling?

Rename $\phi' \to \phi$, $\Gamma' \to \Gamma$, $\Lambda' \to \Lambda$, $\kappa' \to \kappa$, and continue.

b) First, let us study the stability of the homogeneous state. In the Cahn-Hilliard equation, all homogeneous states are stationary. Does the additional reaction term affect this property? Linearize Eq.(4) with respect to the homogeneous density $\bar{\phi}$, find the dispersion relation, and discuss your result. Compare your result to the results from model A and B.

c) Let us now investigate the stability of an inhomogeneous state (phase separated state). Show that the interfacial solution $\phi_{\mathrm{I}}(x) = \tanh\left(\sqrt{\frac{1}{2\kappa}}x\right)$ is a steady state of the 1D system.

d) To investigate the stability of an inhomogeneous state, one can check how a small perturbation $\delta\phi(\mathbf{x})$ on the interface profile affects the free energy. Show that the variation of the free energy with respect to the interfacial profile given by $\delta\mathcal{F} = \mathcal{F}\left[\phi_{\mathrm{I}}(\mathbf{x}) + \delta\phi(\mathbf{x})\right] - \mathcal{F}\left[\phi_{\mathrm{I}}(\mathbf{x})\right]$ to the lowest order is

$$\delta\mathcal{F} = \int_{\mathbb{R}^d} d^d x \left[\frac{(\delta\phi(\mathbf{x}))^2}{2}\left(3\phi_{\mathrm{I}}^2(\mathbf{x}) - 1\right) + \frac{\kappa}{2}\left(\nabla\delta\phi(\mathbf{x})\right)^2\right]. \tag{5}$$

To obtain this result, you need to expand the Ginzburg-Landau functional to the second order. Explain why.

e) Show that in 1D, a small translational perturbation ($\phi = \phi_{\mathrm{I}}(x+\epsilon)$, for small ϵ) with respect to interfacial profile does not increase the total free energy. Why is this perturbation forbidden if reaction terms are absent? What does the result tell you about the stability of the interfacial profile?

f) We would like to investigate the stability of a droplet. Assume that there is a high concentration droplet surrounded by a low concentration bulk. From the lecture, you have learned that due to the surface tension and the curved interface of the droplet, the concentration inside (ϕ_{in}) and outside (ϕ_{out}) is elevated with respect to the local minima

$$\phi_{\mathrm{in/out}} = \phi_{\pm} + \delta\phi_{\pm}\,,$$

where $\phi_+ = 1$ and $\phi_- = -1$. Assume that the deviations are small and there is a length scale separation (width of droplet interface is small compared to scale of density variation). Show that eq.(4) can be reduced to

$$\partial_t\delta\phi_{\pm} = (2\Gamma + \kappa\Lambda)\nabla^2\delta\phi_{\pm} - 2\Lambda\delta\phi_{\pm} \tag{6}$$

for the small deviations inside and outside the droplet. Explain why the equation for the small deviation is the same inside and outside the droplet.

g) Next, we want to use the previously defined eq. (6) to determine the stationary radial profile for a constant radius R of the 3-dimensional droplet in the weak reaction limit $\Gamma \gg \Lambda$. First, sketch the radial profile of the droplet to determine the boundary conditions $\delta\phi_+(0)$, $\delta\phi_+(R)$, $\delta\phi_-(R)$ and $\delta\phi_-(\infty)$. Then use spherical coordinates to show that in the weak reaction limit $\Gamma \gg \Lambda$ the radial profile of the droplet is approximately

$$\phi_{\mathrm{in}} \approx \phi_+ + \delta\phi_{\mathrm{GT}} \tag{7}$$

$$\phi_{\mathrm{out}} \approx \phi_- + \delta\phi_{\mathrm{GT}}\frac{R}{r}. \tag{8}$$

Using your result from part b), explain how the boundary condition $\delta\phi_-(\infty)$ would change without any reactions present.
Hint: Use the Gibbs–Thomson relation from the lecture

$$\delta\phi_{\mathrm{GT}} = \frac{\ell_\gamma^\pm \phi_\pm}{R},$$

where $\ell_\gamma^\pm = \frac{(d-1)\gamma}{(\phi_+ - \phi_-)\phi_\pm f''(\phi_\pm)}$ *is the capillary length, to determine the boundary conditions.*

h) The goal of this last exercise is to determine the radial velocity of the droplet. For this purpose use the stationary radial profile derived in the previous exercise with varying droplet radius $R(t)$. Using the flux balance at the interface, show that in the weak reaction limit $\Gamma \gg \Lambda$ the radial velocity as a function of the droplet size is given by

$$\partial_t R(t) = \frac{-\Gamma l_\gamma^- \phi_-}{R(t)^2}. \tag{9}$$

i) Sketch the radial velocity from the previous part. Compare it to the result derived in the lecture, where you neglected the reaction terms. What is the qualitative difference in the observed droplet behavior?

Exercise 13 – Cahn-Hilliard equation with active reaction

In the previous exercise, the conversion between A and B was driven by thermal equilibrium, meaning it was passive and always minimized the free energy. In contrast, in this exercise, the conversion between A and B is active, driven by an external factor, e.g, consumption of ATP. You will observe in this exercise that fluctuations only grow in a narrow range of length scales, which imply a possible length scale controlling mechanism. Consider the reaction between A and B with forward and backward reaction rates k_1, and k_2 respectively.

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}. \tag{10}$$

The dynamics of the local concentration of A ($c_A = \phi_A/v$) is governed by the Cahn-Hillard equation, modified by a mass-action reaction term.

$$\begin{aligned}\partial_t c_A &= \Gamma\nabla^2 \frac{\delta F\{c_A\}}{\delta c_A} - k_1 c_A + k_2 c_B & (11)\\ &= \Gamma\nabla^2\left(f'(c) - \kappa\nabla^2 c\right) - kc + k(1-c) & (12)\end{aligned}$$

We dropped the subscript "A" in the equation and can write c_B as $(1-c)$. For simplicity, we assume that the forward and backward reactions have the same rate: $k_1 = k_2 = k$ and set the molecular volume to $\nu = 1$.

a) As before, consider the following Ginzburg-Landau free energy functional with a critical density $c_c = \frac{1}{2}$

$$f(c) = -\frac{r}{2}(c - \frac{1}{2})^2 + \frac{u}{4}(c - \frac{1}{2})^4. \tag{13}$$

Linearize Eq. (12) with respect to the homogeneous density $\bar{c}$, find the dispersion relation, and discuss your result.

b) From the exercise, you now understand that the reactions select the initial length scale for growth. However, to fully comprehend the later stages of phase separation, where nonlinearities become significant, we need to investigate the coarsening process by solving the complete nonlinear equation numerically. Use the provided Mathematica notebook with the parameters $r = 1$, $u = 5$, $\Gamma = 1$, and $\kappa = 0.5$. For simplicity, we consider here the one-dimensional system[1]. Initiate the system at $c = 0.5 + \delta c$, where δc is some random fluctuations preset in the notebook. Observe and describe the dynamics in the presence of the reaction.

c) With the same parameter, start the simulation with the initial state as a single droplet, what do you observe now?

d) In the absence of reactions, the 1D Cahn-Hillard system grows logarithmically at late times. i.e, The droplet size growth as

$$L(t) \sim [\ln(t)]^{\alpha} . \tag{14}$$

In the presence of reactions, the droplet size reaches a steady-state. From dimensional analysis, $[t] \sim 1/[k]$. Therefore, the steady-state droplet size should follow the scaling law

$$L_{\infty} \sim [\ln(1/k)]^{\alpha} . \tag{15}$$

Try a few values of $k \in [10^{-4}, 3 \cdot 10^{-4}, 10^{-3}, 3 \cdot 10^{-3}, 0.001, 0.01, 0.03, 0.1]$ and show the relation between steady-state droplet size and k numerically.

Your solutions should be handed in in moodle by **Wednesday, November 19th 2025, 10 am.**

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[1] For snapshots of the two-dimensional system and more detailed information, consider the reference paper (https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.74.2034).