# Phase separation on surfaces in presence of matter exchange
## *Supplementary material*

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## MODEL FOR ONE OR TWO COMPONENTS

As discussed below our model can describe both, matter distributions of one or two components.

### A. One component

Consider first the case of one particle species ($I$). The governing equations are

$$\partial_t n_i - D\nabla^2 n_i = \delta(z)[k_D m_i(\vec{r},t) - k_A n_i(\vec{r}, z=0, t)]$$
$$\partial_t m_i + \vec{\nabla} \cdot \vec{j}_{m_i} = k_A n_i(\vec{r}, z=0, t) - k_D m_i(\vec{r},t), \quad \text{(S.1)}$$

where $i = I$, $m_I$ and $n_I$ are the particle densities on the membrane and in the bulk, respectively. The constants $k_A$ and $k_D$ denote the attachment and detachment rates of particles to and from the membrane, $D$ is the bulk diffusion constant and $\vec{j}_{m_I}$ is the particle current on the membrane. We write $n_I = n_0 + n$ and $m_I = m_0 + m$, where $n_0$ is the particle density infinitely far away from the membrane and $m_0 = k_A n_0/k_D$. The equations for $n$ and $m$ are then the same as Eqs. (1) and (2). Note that when the ratio $k_A/k_D$ is varied one needs to maintain the average density on the surface constant by adjusting the density $n_0$ in the bulk accordingly so that the Ginzburg-Landau (GL) free energy remains symmetrical in $m$. This can always be done except in singular cases such as $k_A = 0$.

The values of $m$ are restricted to $m \geq -m_0$ for the density of membrane-bound particles to be positive. For the values of $\alpha$ and $\delta$ of the GL energy used in the manuscript, we have minima at $m_{1,2} = \mp 1$. Our simulations show that the values of the density $m$ do not exceed the interval $[m_1, m_2]$ such that for $m_0 \geq 1$ the density of membrane-bound particles is positive as required.

### B. Two components

For the two species case, the four governing equations for particles of the two types can be written as in Eq. (S.1) by taking $i = I, II$. In this case, $m_i$ and $n_i$ are

the particle densities of type $i = I, II$ on the membrane and in the bulk, respectively. The constants $k_A$ and $k_D$ denote the attachment and detachment rates of particles $i = I, II$ to and from the membrane. We assume that both particle types attach and detach with the same rates $k_{AI} = k_{AII} = k_A$ and $k_{DI} = k_{DII} = k_D$. Furthermore, we set $\vec{j}_m \equiv \vec{j}_I - \vec{j}_{II} = -\mu \vec{\nabla} \frac{\delta \mathcal{F}}{\delta m}$, such that the dynamic equations for $n = n_I - n_{II}$ and $m = m_I - m_{II}$ are again of the form of Eqs. (1) and (2) of the main text.

The GL form depending on the density differences can be used in the limit when the fluctuations of the difference in density are small compared to the total density on the membrane. This can be done in two ways: either by considering a "three-state problem" or by assuming a constrained density on the membrane.

**GL energy for a "three state" problem**. Let us first consider two independent species. The linear terms can be added and these depend only on the density difference. The main question is whether one can write a GL term that would also depend only on the density difference, knowing that now the total density $n_1 + n_2$ can fluctuate on the membrane given the independence of the two species.

The answer can be obtained by looking at e.g. a spin one model where the three states $\sigma_i = \pm 1$ would represent species $I$ and $II$ and the state $\sigma_i = 0$ would be an empty site. A phenomenological Hamiltonian accounting for the essential features of this situation is

$$H = -J \sum_{(i,j)} \sigma_i \sigma_j - D \sum_j \sigma_j^2, \quad \text{(S.2)}$$

where $(i,j)$ denotes nearest neighbors on some lattice and $D$ is a parameter controlling the proportion of "occupied" versus "empty" sites. We consider $J > 0$ which favours particles of the same species being close to each other. One can derive the GL expression for this Hamiltonian by Feynman's variational approach [1].

Let us denote by

$$T_i = \langle \sigma_i^2 \rangle \quad \text{(S.3)}$$

the density of occupied sites. The difference between the two species is given by

$$m_i = \langle \sigma_i \rangle. \quad \text{(S.4)}$$

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In the mean-field limit, one has for $m_i = 0$

$$T_i = \frac{2e^{D/T}}{1 + 2e^{D/T}}. \tag{S.5}$$

Small deviations from this state can be parametrized by

$m_i$ and $x_i$ with

$$T_i = \frac{2e^{D/T}}{1 + 2e^{D/T}} + x_i. \tag{S.6}$$

A simultaneous expansion in $m_i$ and $x_i$ gives the free energy

$$
\begin{aligned}
\Gamma = & \left[ -T \log\left( 2e^{\frac{D}{T}} + 1 \right) + \frac{1}{4}Tx^2 \left( 3\sinh\frac{D}{T} + 5\cosh\frac{D}{T} + 4 \right) + O\left(x^3\right) \right] \\
& + m^2 \left[ \frac{1}{4}\left(2 + e^{-\frac{D}{T}}\right)T - J + \frac{1}{8}\left( -e^{-\frac{2D}{T}}\left(1 + 2e^{\frac{D}{T}}\right)^2 \right)Tx + O\left(x^2\right) \right] \\
& + m^4 \left[ \frac{1}{96}\left( e^{-\frac{3D}{T}}\left(1 + 2e^{\frac{D}{T}}\right)^3 \right)T + O(x) \right] + O\left(m^5\right)
\end{aligned}
\tag{S.7}
$$

For large values of $D$, the coefficient of the $x^2$ term in Eq. (S.7) is positive and large and thus essentially imposes $x = 0$ i.e. the total density is essentially frozen to its average value. In the same limit, the coefficients of $m^2$ and $m^4$ terms converge to finite values, whereas the term $m^2 x$ is negligible compared to the $m^2$ term (except when extremely close to the transition point). We thus recover the standard GL expansion in terms of the density difference.

**Constrained density on the membrane**. As a second case, let us consider the case where the lipids of the membrane themselves exchange with the environment. Let us assume that the (fluid) lipid membrane consists of two kinds of lipids. The total two-dimensional lipid membrane density $m_{\rm tot}$ is constant, and we denote the densities of lipids in the environment by $n_I$ and $n_{II}$ with $n_{\rm tot} = n_I + n_{II}$ being the total lipid bulk density. Lipid molecules can leave the membrane and new ones can go in. Since $m_{\rm tot} = const$, each leaving lipid is immediately replaced by another lipid molecule from the bulk. In this case, the free energy can be expressed solely in terms of the membrane density $m$ of lipids of type I.

Let $k_d$ denote the rate at which lipid molecules of both kinds leave the membrane. Changes in the density $m$ due to the exchange of lipids with the bulk evolve according to

$$\dot{m} = -k_d m \frac{n_{II}}{n_{\rm tot}} + k_d(m_{\rm tot} - m)\frac{n_I}{n_{\rm tot}}.$$

This rate of change can be expressed in terms of the densities of lipid $I$ only

$$
\begin{aligned}
\dot{m} &= -k_d m \frac{n_{\rm tot} - n_I}{n_{\rm tot}} + k_d(m_{\rm tot} - m)\frac{n_I}{n_{\rm tot}} \\
&\equiv -k_d m + k_a n_I,
\end{aligned}
\tag{S.8}
$$

where $k_a = k_d m_{\rm tot}/n_{\rm tot}$. Since $n_{\rm tot} = const$, Eq. (S.8) has the same form used in the main article.

## REDUCTION OF THE COUPLED DYNAMIC EQUATIONS

The system of two equations for the surface membrane and the reservoir

$$
\begin{cases}
\partial_t n = D\Delta n + \delta(z)[k_D m - k_A n(\vec{r}, z=0, t)] \\
\partial_t m = \mu\nabla^2 \frac{\delta\mathcal{F}}{\delta m} + k_A n(\vec{r}, z=0, t) - k_D m
\end{cases}, \tag{S.9}
$$

can be reduced to a single equation. By defining the Fourier transform of a function $A_x$ as $A_x = \int \frac{dq}{\sqrt{2\pi}} e^{ixq} \tilde{A}_q$, we write

$$\tilde{n}(\vec{q}, z=0, w) = \frac{k_D \tilde{m}(\vec{q}, w)\tilde{I}(\vec{q}, w)}{\sqrt{2\pi} + k_A \tilde{I}(\vec{q}, w)}, \tag{S.10}$$

where $\tilde{I}(\vec{q}, w) = \int dk_z \frac{1}{iw + D(k_z^2 + \vec{q}^2)}$. Replacing (S.10) in (S.9) for $\tilde{I} \neq 0$ we obtain

$$\partial_t m = \mu\nabla^2 \frac{\delta\mathcal{F}}{\delta m} + \mathcal{F}^{-1}\left[ \left( \tilde{K}(\vec{q}, w) - 1 \right) k_D \tilde{m}(\vec{q}, w) \right],$$

with $\tilde{K}(\vec{q}, w) = \frac{1}{\frac{\sqrt{2\pi}}{\tilde{I}(\vec{q}, w)} + k_A}$.

The time-Fourier transform of this quantity is

$$\hat{K}(\vec{q}, t) = \kappa e^{-q^2 Dt}\left( \frac{1}{\sqrt{\pi\kappa t}} - \mathrm{Erfcx}(\sqrt{\kappa t}) \right), \tag{S.11}$$

where $\kappa = \pi\frac{k_A^2}{2D}$, and $\mathrm{Erfcx}(t)$ is the standard error function $\mathrm{Erfcx}(t) = e^{t^2}\frac{2}{\sqrt{\pi}}\int_t^\infty e^{-z^2}dz$.

## NUMERICAL SOLUTION

We discretize Eq. 3 so that the surface particles' density $m$ is a matrix of elements $(i, j)$ at each simulation step $p$, with a given initial condition $m(i, j, p = 0)$. To obtain the evolution of $m$ we use the standard Euler
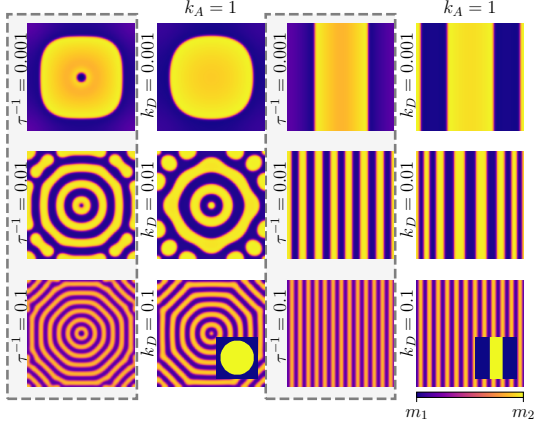
Figure S.1. Snapshot of systems that evolved during $10^4$ simulation steps for different values of the absorption and desorption rates, $k_A$ and $k_D$, respectively, at fixed diffusion constant $D = 0.1$. We consider two different initial conditions (shown on the insets). The effect of matter exchange between the membrane and the bath is observed at relatively short times, especially for larger values of $k_D$. The images highlighted with dashed grey lines correspond to systems that evolved under the instantaneous kernel (Eq. 5).

semi-implicit integration method for the time variable and a five-point discretization of the Laplacian terms in Fourier space for the spatial coordinates.

Compared to a standard Cahn-Hilliard equation we have to consider an extra term involving the integral of our kernel. We approximate the integral in Eq. 3 at a simulation step $p$ by the Riemann sum $\int_0^t dt' \hat{K}(\vec{q}, t - t') m(\vec{q}, t') \simeq \sum_{p'=M}^{p-1} \hat{K}(q_i, q_j, p - p') m(q_i, q_j, p') \Delta t$, where $\hat{K}$ is given by Eq. S.11, and $M$ is the number of previous configurations that will be taken into account in the calculation.

### SHORT-TIME EFFECTS

To further verify the multi-domain state of the system when matter exchange is considered, we studied the cases where the initial condition is a single domain, either a bubble or a stripe, as shown in Fig. S.1. The effect of the kernel is immediately observed in the simulations for both considered kernels.

### SHIFTED POTENTIAL

The Ginzburg-Landau free energy can be shifted $\mathcal{F} = \int d^2 \vec{r} \left\{ -\frac{\alpha}{2}(m - m_c)^2 + \frac{\delta}{4}(m - m_c)^4 + \frac{\gamma}{2}(\nabla m)^2 \right\}$ -as done, for example in [2]. This implies that the initial matter distribution in the membrane is shifted towards one minimum by $m_c$. As a result, the minima of the
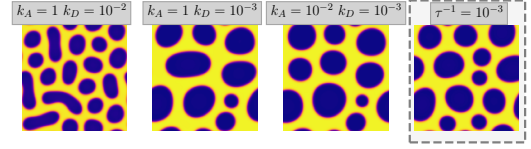


Figure S.2. Simulations were run under the same conditions as in Fig. 2 of the main text: we start from a random initial condition and let the system evolve for $10^5$ steps. We now consider a potential shift $m_c = 0.2$.
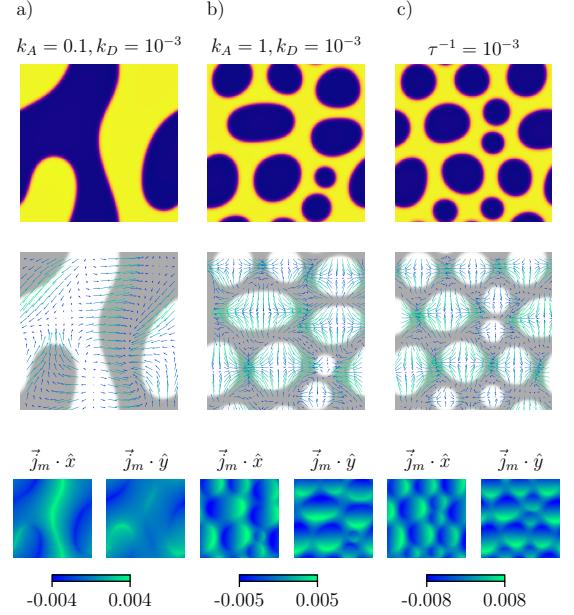


Figure S.3. Top: steady-state configurations observed for a) $k_A = 0.1$ and $k_D = 10^{-3}$ after $10^6$ simulation steps (same as that shown in Figure 2 of our manuscript) b) and c) $k_A = 1$, $k_D = 10^{-3}$ and $\tau^{-1} = 10^{-3}$, respectively, both with shifted potential $m_c = 0.2$ after $10^5$ simulation steps. Central: surface matter current $\mathbf{j}_m = -\mu \vec{\nabla} \frac{\delta \mathcal{F}}{\delta m}$ obtained for the three different configurations. Bottom: surface matter current along the $\hat{x}$ and $\hat{y}$-directions.

double-well potential are shifted towards larger values of $m$ and tilted to favour one minimum. We observe a bubble-like distribution of domains as shown in Fig. S.2.

### MEMBRANE CURRENT

The non-equilibrium character of our system is clearly expressed through the presence of a current of membrane-bound particles in a steady state, see Figure S.3. Due to this current, particles attach to and detach from the membrane at different locations. For $k_a = k_D = 0$, the current vanishes and the system even-

tually settles into an equilibrium state that is globally phase-separated. If one could write the velocity of the membrane-bound particles $\vec{v}$, the current of membrane-bound particles $\vec{j}_m$ written as $\vec{j}_m = \vec{v}m$ would give the length scale of the domains through $v/k_D$.

[1] R. P. Feynman, *Statistical mechanics: a set of lectures* (CRC press, 2018).
[2] L. Foret, EPL (Europhysics Letters) **71**, 508 (2005).