1 Landau Theory of Wetting and Prewetting

2 Overview

Our mean-field theory starts with the Landau Functional shown in Equation 1:

$$\mathcal{L} = \mathcal{L}_{2D} + \mathcal{L}_{3D} \tag{1}$$

$$\mathcal{L}_{2D} = \int d^2\vec{x} f_{2D}(\psi, \rho, \phi_0)$$

$$\mathcal{L}_{3D} = \int d^2\vec{x} dz \frac{1}{2}\nabla\phi^2 + f_{3D}(\phi)$$

$$f_{2D} = \underbrace{\frac{t_{mem}\psi^2}{2} + \frac{u_{mem}\psi^4}{4!} - \lambda_\psi \psi}_{f_{membrane}}$$

$$+ \underbrace{\frac{(\rho - \rho_\star)^2}{\rho_\star} + \frac{(\rho - \rho_\star)^4}{12\rho_\star^3} - \lambda_\rho \rho}_{f_{tether}}$$

$$\underbrace{- h_\psi \rho\psi - h_\phi \rho\phi_0}_{f_{int}}$$

where f_{bulk} is a standard Landau free energy for a two-component system

$$f_{bulk} = \frac{t_{bulk}}{2}\phi^2 + \frac{u_{bulk}}{4!}\phi^4 - \mu_{bulk}\phi \tag{2}$$

3 Our goal is to minimize $\mathcal{L}$ over regard to order parameters ρ,ψ and order parameter profile $\phi(z)$.
4 This requires two derivatives $\frac{\partial\mathcal{L}}{\partial\psi} = \frac{\partial\mathcal{L}}{\partial\rho} = 0$, and a functional derivative $\frac{\delta\mathcal{L}}{\delta\phi(z)} = 0$ which can be
5 thought of as defining how the Landau energy changes as the form of $\phi(z)$ does.

6 Calculating bulk terms and Surface free-energy

7 In Landau theory the bulk energy is a function of the function $\phi(z)$. We sought to simplify
8 calculations to express the bulk energy as a function of initial and final values of ϕ, $\phi(0)$ and $\phi(\infty)$,
9 as these solely determine the behaviour of the density profile. We write $f_{bulk}(\phi) - f_{bulk}(\phi_\infty)$ as
10 $f_{\phi-\phi_{bullk}}$.

First we perform the functional derivative, $\frac{\delta}{\delta\phi(z)}$

$$\mathcal{L}_{bulk}(\phi(z)) = \int dz(f_{\phi-\phi_{bullk}}) + \frac{\nabla\phi^2}{2} \tag{3}$$

$$\delta\mathcal{L}_{bulk}[\phi(z)] = \int_0^\infty dz \frac{\nabla\phi^2}{2}\delta\nabla\phi + f_{\phi-\phi_{bullk}}\delta\phi \tag{4}$$

$$\frac{\delta\mathcal{L}_{bulk}[\phi(z)]}{\delta\phi(z)} = \frac{\partial\mathcal{L}_{bulk}}{\partial\phi} - \nabla\frac{\partial\mathcal{L}_{bulk}}{\partial\nabla\phi}$$

$$= \frac{\partial f_{\phi-\phi_{bullk}}}{\partial\phi} - \nabla^2\phi$$

Now we minimize this to obtain an expression for the energy of spatial gradients, $\nabla\phi$

$$\frac{\delta\mathcal{L}_{bulk}}{\delta\phi(z)} = 0$$

$$\nabla^2\phi = \frac{\partial f_{\phi-\phi_{bullk}}}{\partial\phi}$$

$$\frac{\partial\phi}{\partial z}\nabla^2\phi = \frac{\partial\phi}{\partial z}\frac{\partial f_{\phi-\phi_{bullk}}}{\partial\phi}$$

$$\frac{\partial}{\partial z}(\nabla\phi)^2 = \frac{\partial f_{\phi-\phi_{bullk}}}{\partial z}$$

$$\frac{1}{2}\int_{z=0}^{z=\infty}\frac{\partial}{\partial z}\nabla\phi^2 = \int_{z=0}^{z=\infty}\frac{\partial}{\partial z}f_{\phi-\phi_{bullk}}$$

$$\frac{1}{2}(\nabla\phi_\infty^2 - \nabla\phi_0^2) = f_{\phi-\phi_{bullk}}(\phi_\infty) - f_{\phi-\phi_{bullk}}(\phi_0)$$

$$(\nabla\phi_\infty = 0, f_{\phi-\phi_{bullk}}(\phi_\infty) = 0)$$

$$\frac{1}{2}\nabla\phi^2 = f_{\phi-\phi_{bullk}}(\phi)$$

$$\nabla\phi = \pm\sqrt{2f_{\phi-\phi_{bullk}}(\phi)} \tag{5}$$

11   The sign of 8 depends on whether ϕ_0 is above or below ϕ_∞: polymer density should always move
12   towards the bulk equilibrium density.

Finally we substitute this into our original functional and rewrite as an integration over values
of ϕ rather than coordinates z

$$\mathcal{L}_{bulk}(\phi(z)) = \int_0^\infty dz\frac{1}{2}\nabla\phi^2 + f_{\phi-\phi_{bullk}}$$

$$\mathcal{L}_{bulk}(\phi(z)) = \int_0^\infty dz\nabla\phi^2 \tag{6}$$

$$= \int_{\phi_0}^{\phi_{bulk}} dz\frac{d\phi}{dz}\frac{dz}{d\phi}\nabla\phi^2$$

$$= \int_{\phi_0}^{\phi_{bulk}} d\phi\nabla\phi$$

$$\mathcal{L}_{bulk}(\phi_0,\phi_\infty) = \int_{\phi_0}^{\phi_{bulk}} d\phi\sqrt{(2(f_{\phi_0} - f_{\phi_{bulk}}))} \tag{7}$$

Where we may now minimize the free energy over values of ϕ_0, ρ, and ψ and compute the energy
of each of these solutions. This can be expressed as

$$\mathcal{L} = \mathcal{L}_{bulk}(\phi_0,\phi_\infty) + \mathcal{L}_{2D}(\phi_0,\psi,\rho)$$

$$= \int_{\phi_0}^{\phi_{bulk}} d\phi\sqrt{2(f_{\phi_0} - f_{\phi_{bulk}})} + \mathcal{L}_{2D}$$

We can write this equivalently as

$$\mathcal{L} = \int_{\phi_0}^{\phi_{bulk}} d\phi\left\{\nabla\phi - \frac{\partial f_{2D}}{\partial\phi}\right\} + \frac{\partial f_{2D}}{\partial\phi}|_{\phi_\infty}$$

13   where the final equation is the is the integration between the curves of $\nabla\phi$ and $-\frac{\partial f_{2D}}{\partial\phi_0}$ shown in
14   Figure 4B.

Critical enhancement of Prewetting Regime

The accumulation of polymer and tether density near the critical point is explained in analogy to the susceptibility of an Ising model near it's own critical point. How can this be seen through the Landau equations? First we simplify the membrane and tether components of our Hamiltonian to only contain quadratic terms, and obtain expressions for minimal values of ψ and ρ

$$\frac{\partial f_{2D}}{\partial \psi} = \frac{\partial f_{2D}}{\partial \rho} = 0$$

$$\psi_{min} = -\frac{h_\psi \lambda_\rho \rho_\star + h_\psi \rho_\star + h_\psi h_\phi \rho_\star \phi_1 + \lambda_\psi}{h_\psi^2 \rho_\star - t_{mem}}$$

$$\rho_{min} = -\frac{t_{mem} h_\phi \rho_\star \phi_1 + t_{mem} \lambda_\rho \rho_\star + t_{mem} \rho_\star + h_\psi \lambda_\psi \rho_\star}{h_\psi^2 \rho_\star - t_{mem}}$$

Which we substitute into the original f_{surf}

$$f_{surf}(\phi_0, \psi, \rho) = \mathcal{L}_{3D}(\phi_0, \phi_{\inf}) - \frac{t_{mem} h_\phi^2 \rho_\star}{2(t_{mem} - h_\psi^2 \rho_\star)}\phi_1^2 + \frac{h_\phi \rho_\star (t_{mem}\lambda_\rho + t_{mem} - h_\psi \lambda_\psi)}{t_{mem} - h_\psi^2 \rho_\star}\phi_1 \tag{8}$$

$$- \frac{\rho_\star \left(t_{mem}\lambda_\rho(\lambda_\rho + 2) + h_\psi^2 \rho_\star\right) - 2h_\psi(\lambda_\rho + 1)\lambda_\psi \rho_\star + \lambda_\psi^2}{2\left(t_{mem} - h_\psi^2 \rho_\star\right)}$$

Here we can see that second order couplings in ϕ_0 emerge when f_{2D} is minimized over membrane and tether degrees of freedom. Including fourth order membrane and tether terms gives higher order terms in ϕ_0. All of these terms have a similar denominator, $t_{mem} - h_\psi^2 \rho_\star$, that can be identified as the membrane critical point, $J_{c,mem}$ subject to the insertion of tethers. We can see that the surface free energy diverges as we approach the critical coupling. The surface enhancement is proportional to $(J_{c,mem} - J_{mem})^{-1}$ which is consistent with the scaling of the Ising model susceptibility exponent $\gamma = 1$ in mean-field.

Susceptibility terms Enters Equations

The susceptibility of the membrane enters How can we see that the critical point enhancement is a symptom of a large susceptibility? We can rewrite $\mathcal{L}_{2D}$ with an emphasis on the interaction terms

$$\mathcal{L}_{2D} = \int d^2\vec{x}\{f_{mem}(\psi) + f_{tether}(\rho) - h_\psi \psi \rho - h_\phi \phi_0 \rho\} \tag{9}$$

We take the mean-field over the energy terms, $\langle f_{tether}\rangle$, $\langle f_{mem}\rangle$, which we assume provide non singular contributions to the free energy. We expand the interaction terms, $\mathcal{L}_{int}$:

$$\mathcal{L}_{int} = \langle\mathcal{L}_{int}\rangle - \frac{1}{2}\langle\mathcal{L}_{int}^2\rangle + \ldots$$

$$= \int d^2\vec{x} h_\psi \psi \rho + h_\phi \phi_0 \rho$$

$$- \frac{1}{2}\int d^2\vec{x}\int d^2\vec{x'}\{\rho\rho'(h_\psi \psi\psi' + h_\phi \phi_0 \phi_0')\}$$

3

We assume the membrane is at it's critical composition and above it's critical point, so $\psi = 0$, and additionally that tethers and bulk are far from a critical point so we can use their average values

$$\langle \mathcal{L}_{int} \rangle = \langle \rho \rangle (h_\phi \langle \phi_0 \rangle + h_\psi \langle \psi \rangle)$$

$$\langle \mathcal{L}_{int}^2 \rangle = -\frac{\langle \rho \rangle^2}{2} h_\psi^2 \int d^2 \vec{x} \int d^2 \vec{x}' \psi_x \psi_{x'}$$

$$= -\frac{\langle \rho \rangle^2}{2} h_\psi^2 \int d^2 \vec{x} \int d^2 \vec{x}' \langle \psi_x \psi_{x-x'} \rangle - \langle \psi_x \rangle^2$$

$$= -\frac{\langle \rho \rangle^2}{2} h_\psi^2 \int d^2 x \int d^2 x' G(x - x')$$

$$= -\frac{\langle \rho \rangle^2}{2} h_\psi^2 A \int d^2 r G(r)$$

$$= -\frac{\langle \rho \rangle^2}{2} h_\psi^2 \chi_\psi$$

Where χ_ψ is the susceptibility of the membrane and $G(r)$ is the two-point correlation function. The second to last step assumes that $G(x - x')$ is translationally invariant. The relationship between χ_ψ and $G(r)$ is known as the static susceptibility sum rule. At the critical point $\psi = 0$. We can assume fluctuations in ϕ_0 are small

$$\mathcal{L}_{int} = \langle \rho \rangle \left(-h_\phi \langle \phi_0 \rangle - \frac{\langle \rho \rangle}{2} h_\psi^2 \chi_\psi \right) \tag{10}$$

At the critical point, $\chi_\psi \to \infty$, implying that interactions become very favorable even with negligible contributions from other terms. Substituting this as f_{int} in our original free energy functions, and recalling that the integral over the correlation function above integrates out the membrane degrees of freedom, we obtain a new free energy function, neglecting fourth order terms:

$$f_{2D} = \frac{(\rho - \rho_\star)^2}{\rho_\star} - \lambda_\rho \rho - h_\phi \phi_0 \rho - \frac{h_\psi^2 \rho^2}{2} \chi_\psi \tag{11}$$

Minimizing over ψ and ρ, and substituting back in the free energy, as above, we obtain our free energy functions in terms of ϕ_0

$$f_{2D} = -\frac{h_\phi^2 \rho_\star}{2(h_\psi^2 \rho_\star \chi_\psi - 1)} \phi_0^2 + \frac{h_\phi(1 + \lambda_\rho \rho_\star)}{h_\psi^2 \rho_\star \chi_\psi - 1} \phi_0 + \frac{\rho_\star(h_\psi^2 \rho_\star \chi_\psi + \lambda_\rho^2 + 2\lambda_\rho)}{2(h_\psi^2 \rho_\star \chi_\psi - 1)} \tag{12}$$

Where this is similar to equation 8, where the denominator goes to zero at the membrane critical point $\chi_\psi = \frac{1}{h_\psi^2 \rho_\star}$. This makes two predictions. First that the membrane critical point is shifted to $t_{mem} = (h_\psi^2 \rho_\star)^{1/\gamma}$; shifting this to slightly higher values of t_{mem} than in mean field, and making the divergence more pronounced with the 2D Ising susceptibility exponent γ being 7/4 when calculated exactly.
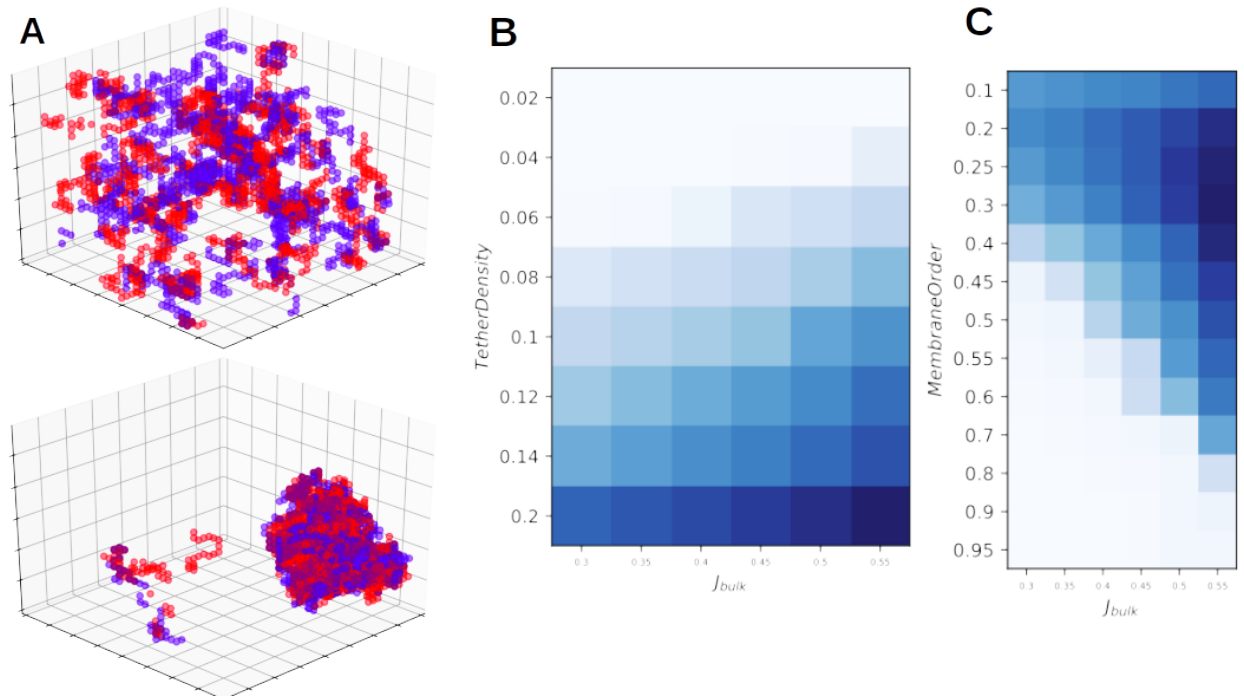
1 Supplemental figures

Figure 1: **Monte-Carlo Simulations A**) Lattice polymer simulations show phase coexistence. Simulations at $0.25k_BT$ have homogeneous polymer density, top. Simulations at strong polymer coupling $1.0k_BT$, bottom, see coexisting dense and dilute phases. **B**) Increasing tether density increases polymer density on the membrane **C**) More disordered membranes increase polymer density on the membrane
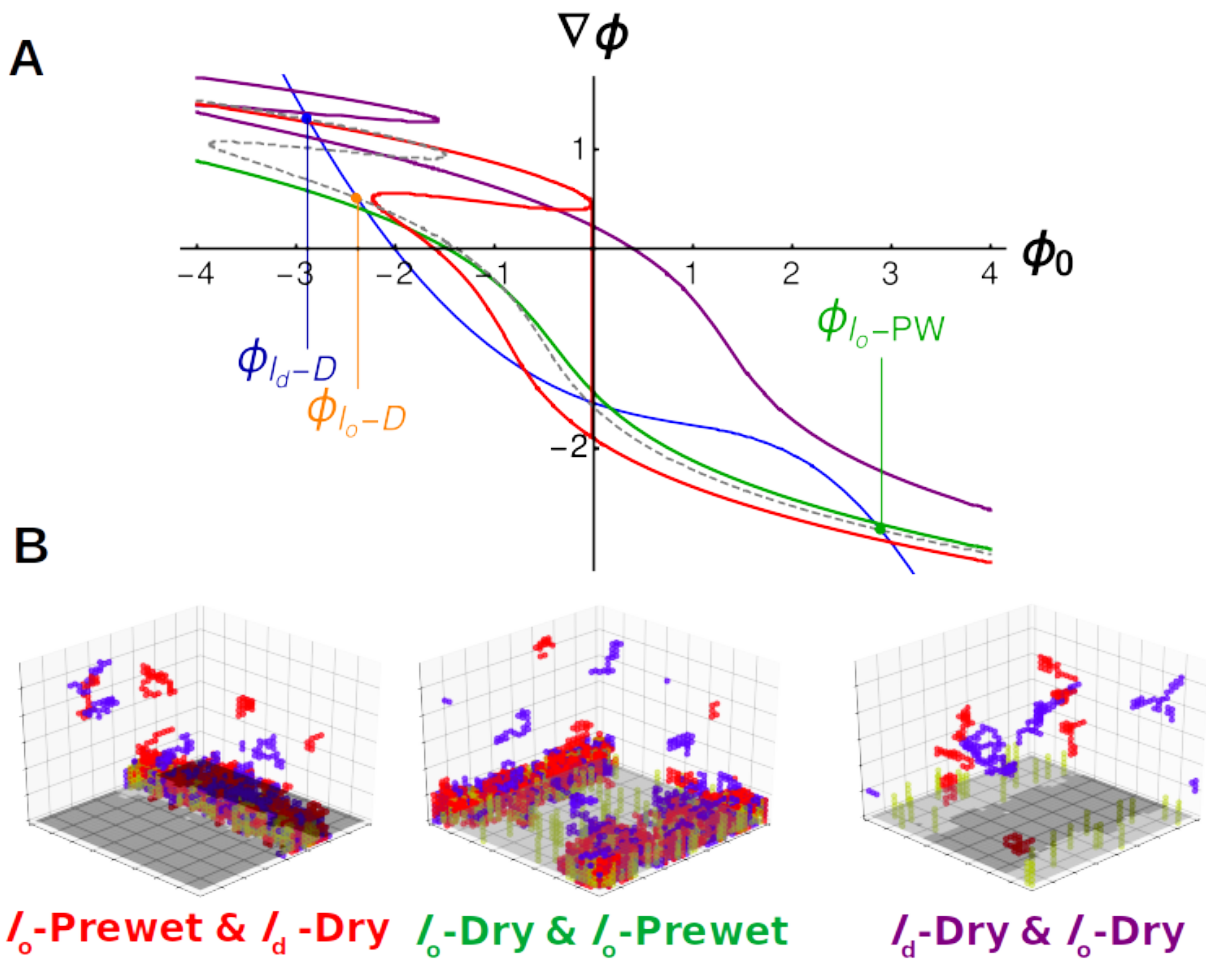
Figure 2: **Two-phase coexistence near three-phase coexistence A**) Gradient construction within each two phase region depicted in Figure 6A. **B**) Two-phase coexistence regions observed in simulation
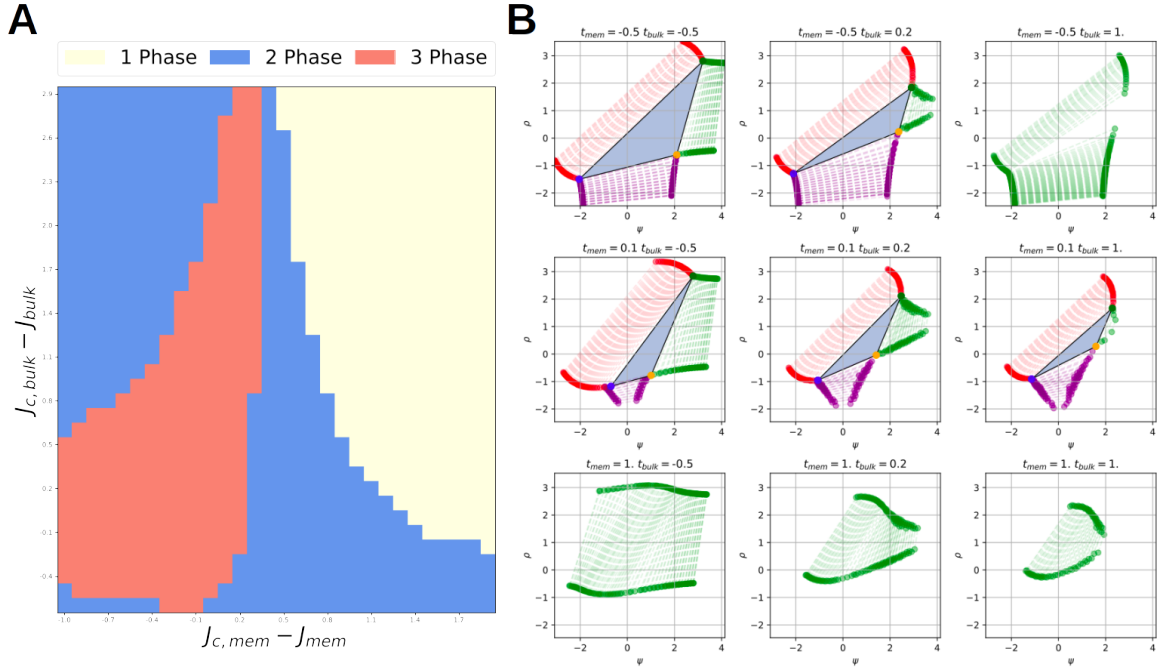
Figure 3: **Bulk and Membrane Coupling govern 3-phase coexistence A**) Phase diagram over membrane and bulk couplings showing one, two, and three phase regions (yellow, blue, and red). Three phase coexistence generally requires strong membrane and bulk interactions, but extends to weaker J_{bulk} near the membrane critical point. **B**) Surface phase diagrams at various membrane and bulk couplings. Weak membrane couplings collapse the purple (l_0-dry,l_d-dry) region, top to bottom. Weak bulk couplings shrink the green (l_o-prewet,l_o-dry) edge, left to right.