Geometric Evolution of Bilayers under the Functionalized Cahn-Hilliard Equation

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We employ a multiscale analysis to derive a sharp interface limit for the dynamics of bilayer structures of the Functionalized Cahn-Hilliard equation. In contrast to analysis based upon single-layer interfaces, we show that the Stefan and Mullins-Sekerka problems derived for the evolution of single-layer interfaces for the Cahn-Hilliard equation, [Pego (1989)] are trivial in this context, and the sharp interface limit yields a quenched mean-curvature driven normal velocity at $O(\varepsilon^{-1})$ while on the longer $O(\varepsilon^{-2})$ time scale it leads to a total-surface-area preserving Willmore flow. In particular, for space dimension $n=2$, the constrained Willmore flow drives collections of spherically symmetric vesicles to a common radius, while for $n=3$ the radii are constant, and for $n \geq 4$ the largest vesicle dominates.

1. Introduction

The Functionalized Cahn-Hilliard (FCH) equation has been proposed as a model for interfacial energy in phase separated mixtures with an amphiphilic structure [Gompper and Schick (1990)]. Of particular interest are polymer-electrolyte membranes in which hydrophobic polymers are functionalized by the addition of acid-tipped side chains which greatly modify their solubility, [Promislow & Wetton (2009), Gavish et al. (2011), Gavish et al (2012)]. In particular the solvation energy of the tethered acid groups drives the mixture to *increase* surface area so as to facilitate the access of the side-chains to the solvent phase whose screening effect serves to lower the overall electrostatic energy, [Gompper and Schick (1990)]. In addition, there is considerable interest in the properties of bilayer structures within the biological community, where issues such as endocytosis, vesicle budding, and the opening of pores are of interest, [Budin & Szostak (2011), Zhu et al (2012)].

The FCH energy is a natural test-bed for the study of bilayer structures. In contrast to models based upon single layer or heteroclinic interfaces with no intrinsic bending energy, the FCH naturally produces stable bilayer, or homoclinic, interfaces with an intrinsic width which is resistant to external forces. Moreover, unlike sharp interface approximations such as the Canham-Helfrich energy, [Canham (1970), Helfrich (1973)], the FCH naturally accommodates merging and pinch-off events which are dominant mechanisms for formation of networks.

The Cahn-Hilliard (CH) energy, introduced in [Cahn & Hilliard (1958)], characterizes a binary mixture by a phase field function u which maps $\Omega \subset \mathbf{R}^n$ into

Proc. R. Soc. A 1–24; doi: 10.1098/rspa.00000000
March 4, 2013

mixture values $[-1,1]$. It models the free energy as a balance between entropic effects, which seek to homogenize the species, and the mixture potential, W, which assigns energies to blends

$$\mathcal{E}(u) = \int_\Omega \frac{\varepsilon}{2}|\nabla u|^2 + \varepsilon^{-1} W(u)\, dx, \tag{1.1}$$

where the parameter $\varepsilon \ll 1$ controls the width of the inner structures. Motivated by the study [Gavish et al. (2011)], we consider a class of double-well potentials, W, which describes the energy of the mixture u, with two *unequal depth* local minima at $b_- < b_+$, for which $W(b_-) = 0 > W(b_+)$, and W' has precisely three zeros, at $b_- < b^0 < b_+$. The phase $u = b_-$ with the higher self-energy is the majority phase, while the $u = b_+$ phase is the minority phase (amphiphilic surfactant or lipid). The well-tilt, or difference in self-energies $W(b_-) - W(b_+) > 0$, is a significant bifurcation parameter for network morphologies, [Gavish et al (2012)].

The single layer interfaces of the Cahn-Hilliard free energy are natural minimizers of $\mathcal{E}$ for untilted wells W, i.e. $W(b_-) = W(b_+)$. Solutions generated from single layer interfaces are well-known to Γ-converge to interfacial surface area as $\varepsilon \to 0$, [Modica (1987), Sternberg (1988)]. That is, for $\varepsilon \ll 1$, minimizing sequences u_ε which converge to a limit in $L^1(\Omega)$ localize their gradients on an interface $\Gamma \subset \mathbf{R}^n$ while $\mathcal{E}(u_\varepsilon)$ tends to a value which is proportional to the interfacial surface area. The FCH remaps this paradigm, balancing the square of the variational derivative of the CH energy against a small multiple of itself,

$$\mathcal{F}(u) := \int_\Omega \frac{1}{2}\left(\frac{\delta \mathcal{E}}{\delta u}\right)^2 dx - \varepsilon \eta_2 \mathcal{E}(u). \tag{1.2}$$

The term functionalization is borrowed from synthetic chemistry where it refers to the addition of hydrophilic (functional) groups to a hydrophobic polymer to modify its solubility. Mathematically, "functionalization" is a systematic reformulation of the original energy. Indeed for the $\eta_2 = 0$ problem, <u>all</u> critical points of $\mathcal{E}$, that is the solutions of $\frac{\delta \mathcal{E}}{\delta u} = 0$, render $\mathcal{F}(u) = 0$ and hence are global minimizers of $\mathcal{F}$. The parameter η_2 unfolds this highly degenerate situation: crucially, for $\eta_2 > 0$, the unfolding term *favors* the critical points of $\mathcal{E}$ with more surface area. For the particular form of the CH energy, the FCH takes the form,

$$\mathcal{F}(u) = \varepsilon^{-2} \int_\Omega \frac{1}{2}\left(-\varepsilon^2 \Delta u + W'(u)\right)^2 - \varepsilon^2 \eta_2 \left(\frac{\varepsilon^2}{2}|\nabla u|^2 + W(u)\right) dx. \tag{1.3}$$

There is an extensive literature which employs single-layer interfaces to describe a wide range of physical phenomena including image segmentation, phase transitions, multi-phase flows, crystallization, and other phase transitions. Higher order energies, which resemble the FCH with $\eta_2 < 0$ and an untilted well W, have been proposed, see in particular equations (1.5) of [Loreti & March (2000)] and (3.16) of [Torabi et al (2009)]. Indeed, the De Giorgi conjecture, which concerns the Γ limit of the FCH energy for $\eta_2 < 0$ with an untilted well has been established, [Roger & Schatzle (2006)]. Extensions of these models to address deformations of elastic vesicles subject to volume constraints, [Du et al (2004)], [Du et al (2006)], and multicomponent models which incorporate a variable intrinsic curvature have been investigated, [Wang and Du (2008)], [Lowengrub et al (2009)]. However, the single-layer interface forms the essential underpinning of each of these models. Conversely, it is easy to see that for $\eta_2 > 0$ the FCH energy does not have an

ε independent lower bound over configurations with prescribed volume fraction. In this regime the FCH has no traditional Γ-limit, and the natural tendency to view the FCH energy as a diffuse interface regularization of a Canham-Helfrich, [Canham (1970), Helfrich (1973)] sharp interface energy of the form

$$\mathcal{E}_{\mathrm{CH}}(\Gamma) := \int_\Gamma a_1 H^2 - a_2 \, dS, \tag{1.4}$$

is potentially misleading. The identification of the FCH with a Canham-Helfrich type sharp interface energy is predicated on the assumption that the underlying structures are of co-dimension 1 and free of defects, such as end-caps and junctions. Over $\mathbb{R}^3$ the FCH free energy supports co-dimension one bilayer interfaces, whose evolution we study here, as well as and a wide range of stable co-dimension 2 and co-dimension 3 morphologies, [Doelman and Promislow (2013), Gavish et al (2012)], described below, in addition to many locally stable defect structures. The structure of the problem, and the physically motivating examples, change fundamentally and dramatically with the sign of η_2. For these reasons the FCH merits a distinct name, see [Promislow & Wetton (2009)], which evokes the amphiphilic nature of functionalized polymers.

It is crucial to emphasize the distinction between single-layer interfaces, which separate two dissimilar phases across a co-dimension one interface, and bilayers which separate two identical phases by a thin region of a second phase. *Significantly, the single-layer framework cannot support perforation of the interface.* In many biological processes it is essential to understand the opening and closing of pores within a vesicle, or the roll-up of a bicelle into a closed vesicle, [Shinoda et al (2011)]. Single layer models treat the inside and outside of a vesicle as distinct phases: they cannot be merged. In contrast, the $\eta_2 > 0$ unfolding of the tilted-well FCH model supports stable, strongly incompressible bilayers which admit not only the opening of perforations, but the roll-up of the bilayer into a solid filament or a solid micelle, in a manner which naturally accounts for the competition between these morphologically distinct structures for a scarce surfactant phase. We do not fully address this competition within the current work, rather we demonstrate that the sharp interface limit of the FCH energy for bilayer structures has fundamental distinctions with the sharp interface limit derived for single layers, see (1.8) and the following discussion.

The essential feature of functionalization is that it greatly increases the possible collection of stable interfacial structures. For the CH energy, the quasi-stable structures are dominated by non-self-intersecting, smooth, co-dimension one, closed interfaces, $\Gamma \subset \Omega$. The normal and tangential spaces of Γ form a coordinate system in a neighborhood about Γ, in which at leading order the cartesian Laplacian becomes $\varepsilon^2\Delta = \partial_z^2 + O(\varepsilon)$ where $z = z(x)$ is the inner variable, often presented as the $\varepsilon-$scaled, signed distance to the interface. Subject to a total mass constraint, the co-dimension one critical points of the CH energy are constructed from inner structures solving the second-order differential equation

$$\partial_z^2 U - W'(U) = \lambda. \tag{1.5}$$

Choosing the Lagrange multiplier λ so that the modified well $W(s) + \lambda s$ is 'un-tilted', i.e. taking equal values at its two minima, then (1.5) supports a heteroclinic or single-layer connection, U_s between the two minima. The interface

Γ is then "dressed" with U_s, see (2.11), yielding an approximate critical point of $\mathcal{E}$ which takes distinct constant values on the regions on the opposite sides of the interface Γ. It is significant that the squared-variational term within the FCH prevents the Lagrange multiplier associated to the mass constraint from 'un-tilting' the well W, rather the multiplier serves to shift the location of the two minima, particularly that of the majority phase to $b = b_- + O(\varepsilon)$, see (5.10) and [Gavish et al. (2011)]. As a consequence, there is a bilayer solution $U_b = U_b(z;\lambda)$ of (1.5) with $\lambda = 0$ which is homoclinic to the shifted majority phase b, potentially stable, [Doelman and Promislow (2013)].

For a co-dimension one interface, Γ, the dressing of Γ with U_b yields to a bilayer interface with an $O(\varepsilon)$ width which is potentially stable, coherent structure, [Doelman and Promislow (2013)]. Moreover, stable structures can also be generated near higher co-dimensional interfaces. For example in $\mathbf{R}^3$, co-dimension two structures are formed by dressing a one dimensional filament Γ with a radially symmetric solution of

$$\partial_R^2 U + \frac{1}{R}\partial_R U - W'(U) = 0, \tag{1.6}$$

where $R > 0$ is the scaled distance to the center line of Γ. The end result is a 'spaghetti' like structure with an $O(\varepsilon)$ unscaled radius, but a spatially extended length. The FCH also possesses co-dimension three micellular structures in $\mathbf{R}^3$ as well as defect states such as end-caps and multi-junctions which play an essential role in network formation, see [Gavish et al (2012)] and [Dai and Promislow (2013)].

This paper presents a formal reduction of the H^{-1}−gradient flow of the functionalized energy $\mathcal{F}$, called the Functionalized Cahn-Hilliard equation,

$$u_t = \varepsilon^2 \Delta \frac{\delta \mathcal{F}}{\delta u} = \Delta \overbrace{\left(-\varepsilon^2\Delta + W''(u) - \varepsilon^2\eta_2\right)\left(-\varepsilon^2\Delta u + W'(u)\right)}^{\mu}, \tag{1.7}$$

subject to periodic or zero-flux boundary conditions on $\Omega \subset \mathbf{R}^n$. Here μ is the chemical energy. This flow has the distinction of decreasing $\mathcal{F}$ while preserving the masses of the majority and minority (surfactant) phases via a flux law that depends locally on the values of concentration u. One may anticipate that solutions of the FCH equation quickly converge towards a slow-manifold comprised of approximate critical points of $\mathcal{E}$ and, modulo self-intersection or pinch-off events of the underlying interface, subsequently flow slowly along the manifold until arriving at a morphology of approximate critical points of $\mathcal{E}$ whose surface area is maximal in comparison to other approximate critical points of $\mathcal{E}$.

Our central results confirm this intuition, however there are several surprises. Indeed, for the single-layer interfaces of the Cahn-Hilliard equation, it was shown, [Pego (1989)] that the sharp interface reduction yields a spinodal decomposition at $O(\varepsilon^{-1})$, a Stefan-problem, at $t = O(1)$, and a Mullins-Sekerka problem, at $t = O(\varepsilon^{-1})$, for the outer chemical potential. In contrast, for the choice of scaling in (1.7) the flow is slower, but more importantly the chemical potential problem *uncouples from the free surface problem*; the chemical potential converges to a spatial constant, and the free-surface problems reduce to Ricci-type flows. Indeed on the $O(\varepsilon^{-1})$ time scale, in place of the Mullins-Sekerka problem, we find a quenched mean-curvature driven flow, in which the normal velocity couples to an evanescent, spatially constant, chemical potential, $B_1(t_1)$,

$$V_n = \sigma_1 B_1(t_1)\kappa_0, \tag{1.8}$$

$$\frac{d}{dt_1} B_1 = -\frac{\rho_1}{|\Omega|} B_1 \int_\Gamma \kappa_0^2(s)\, ds, \tag{1.9}$$

where κ_j, introduced in (2.8) is the sum of the $j+1$-st powers of the curvatures, while the W dependent constants $\sigma_1, \rho_1 > 0$ are surface tensions and decay rates.

While the exponential decay of B_1 quenches the mean-curvature flow, the sign of B_1, see (5.30), is of significance. The equilibrium value, b_-, of the majority phase, i.e. the left minima of the double well W, is associated to a mixture with a small, positive concentration of the minority phase (typically amphiphilic surfactant or lipid). The case $B_1 > 0$ corresponds to an initial mass of the minority phase in excess of that required to construct the prescribed initial interface Γ_0 with $u = b_-$ far from the interface. That is, the mass constraint is such that the adjusted background state $b > b_-$. Conversely, $B_1 < 0$ corresponds to a deficit in the initial mass of the minority phase: to construct the prescribed initial interface Γ_0 the value b of u far from the interface satisfies $b < b_-$. An analysis of the FCH shows that the excess surfactant configurations are strongly unstable, as growth of interface leads not only to a lower energy through the η_2 term, but drives the background concentration towards equilibrium. On the other hand, the deficit situation, $B_1 < 0$, is a more stable balance, with growth of interface limited by the expense of further reductions in the far-field value, b, of u.

This dichotomy is consistent with the normal velocity given in the sharp interface reduction (1.8). For $B_1 > 0$ the mean-curvature flow is ill-posed as an evolution problem, leading to uncontrolled growth of interface, while for $B_1 < 0$ it is well-posed in time with possible finite-time singularities associated to "contraction" of isolated vesicles as their surfactant phase is absorbed into the background state and possibly redistributed to other structures. For $B_1 < 0$ the exponential decay of B_1 to zero quenches this fast transient. For $B_1 > 0$ the quenching is even faster, however the ill-poseness of the curvature flow removes us from the framework of the formal analysis presented herein. This dichotomy has no analogy within the single layer models, but is compatible with experimental observations, particularly [Budin & Szostak (2011)] in which the addition of a small background component of oleate (lipid) into a suspension of phosphate containing vesicles lead to the spontaneous destabilization of the vesicles to an uncontrolled filamentation process. Indeed, the authors of that work propose the destablization as a mechanism for cell division in primitive vesicles.

In the deficit situation, $B_1 < 0$ approaches zero, initiating the slower $O(\varepsilon^{-2})$ time-scale. Here the chemical potential again uncouples from the interface Γ, which evolves under the *interface preserving* normal velocity

$$V_n = \sigma_2 \Pi_\Gamma \left[\left(\Delta_s + \frac{\kappa_0^2}{2} - \kappa_1 \right) \kappa_0 \right], \tag{1.10}$$

where Π_Γ, introduced in (6.31) is a zero-average, curvature weighted projection and $\sigma_2 > 0$ is a surface tension depending only upon W. The interface-preservation property is a direct consequence of the incompressibility of the bilayer structure and the mass constraint which fix the total interfacial width. This is distinct from sharp interface reductions of single layer models. Indeed, the normal velocity generated by an H^{-1} gradient flow of the Cahn-Hilliard energy (1.1) couples to a Mullins-Sekerka problem for the chemical potential, [Pego (1989)], while the L^2 gradient flow of an FCH type energy yields a Willmore type flow, but for which the quantity of interfacial material, the minority phase of the FCH, is not conserved, [Loreti & March (2000)]. In particular, the interface preserving Willmore flow generated by bilayer structures yields markedly different evolution in space dimension $n=2$, $n=3$ and for $n \geq 4$, see (6.35).

2. The whiskered coordinates and innerexpansions

The FCH equation possesses many regimes and a global analysis of the PDE is not reasonable. We assume an initial state that starts within a neighborhood of a bilayer interface. More specifically we assume that we have a smooth, co-dimension one initial interface $\Gamma_0 \subset \mathbb{R}^n$, which divides $\Omega = \Omega_+ \cap \Omega_-$ into an interior Ω_+ and an exterior Ω_-, given parametrically, at least locally, by

$$\Gamma_0 = \{\phi_0(s) : s = (s_1, \ldots, s_{n-1}) \in Q_0 \subset \mathbb{R}^{n-1}\}, \tag{2.1}$$

where $\phi_0 : Q_0 \subset \mathbb{R}^{n-1} \mapsto \mathbb{R}^n$ is smooth. We will describe the geometric evolution of the bilayer interfaces as a flow in time t on this space, yielding a curve $\Gamma(t)$ parametrized by $\phi(s,t)$ over a set $Q(t)$. The bilayer solutions we consider are expressed in the normal-tangential coordinate system in a neighborhood of $\Gamma(t)$.

For simplicity we choose the parametrization so that s_i corresponds to arc length along the i^{th} coordinate curve and the coordinate curves are lines of curvature. In this setting the vectors $\mathbf{T}^i = (T_1^i, \ldots, T_n^i)$ defined by

$$\mathbf{T}^i := \frac{\partial \phi}{\partial s_i}, \quad i = 1, \ldots, n-1 \tag{2.2}$$

form an orthonormal basis for the tangent space to Γ at $\phi(s,t)$. Denoting the outer normal vector of Γ pointing towards Ω_- by $\mathbf{n}(s,t) = (N_1, \ldots, N_n)$, we have the relations

$$\frac{\partial \mathbf{T}^i}{\partial s_i} = -k_i \mathbf{n}, \quad \frac{\partial \mathbf{n}}{\partial s_i} = k_i \mathbf{T}^i, \quad i = 1, \ldots, n-1 \tag{2.3}$$

where $k_i = k_i(s)$ are principal curvatures of Γ at $\phi(t,s)$.

From the implicit function theorem, for each x_0 on Γ there exists a neighborhood $\mathcal{N}_{x_0}$ of Γ, with the property that the map $x \mapsto (s,r)$ defined by

$$x = \phi(s,t) + r\mathbf{n}(s,t) \tag{2.4}$$

is locally and smoothly invertible for each fixed time t. In particular in this neighborhood we have the functions $s = s(x)$ and $r = r(x)$ that relate the local coordinates to the cartesian ones. We introduce the scaled coordinate $z = \frac{r}{\varepsilon}$ and the "whiskers"

$$w(s) := \left\{ \phi(s) + z\mathbf{n}(s) \middle| \, z \in [-\ell/\varepsilon, \ell/\varepsilon] \right\}, \tag{2.5}$$

which correspond to line segments of length ℓ, in unscaled distance, emanating from Γ in the normal direction. From the implicit function theorem, for ℓ sufficiently small, these whiskers do no self-intersect locally in s. We say that an interface Γ is far from self intersection if there exists $\ell > 0$ such that none of the whiskers of length ℓ intersect each other or $\partial\Omega$. We introduce the neighborhood

$$\Gamma_\ell = \bigcup_{s\in Q} w(s) \tag{2.6}$$

of Γ, which comprises all points $x \in \Omega$ that are within a distance ℓ of Γ.

The proof of the following lemma, which summarizes the properties of the coordinate system, can be found in, [Cahn, Elliott & Novick-Cohen (1996), Dai and Du (2012), Gavish et al. (2011), Pego (1989)].

Lemma 1. *Let $\Gamma = \Gamma(t)$ be a smooth interface of the form (2.1) with curvatures $\{k_i\}_{i=1}^{n-1}$ uniformly $O(1)$. The normal velocity V_n of Γ at $\phi(s,t)$ is given by $-\partial_t r(s,t)$, and the tangential coordinates (r,s) enjoy the properties*

$$\nabla_x s_i = \frac{1}{1+rk_i}\mathbf{T}^i, \quad \Delta_x s_i = -\frac{r}{(1+rk_i)^3}\frac{\partial k_i}{\partial s_i}, \quad i = 1,\dots,n-1,$$

$$\nabla_x r = \mathbf{n}, \quad \Delta_x r = \sum_{j=1}^{n-1}\frac{k_j}{1+rk_j}.$$

In particular in the scaled (z,s) coordinates we may expand the Cartesian Laplacian in terms of the Laplace-Beltrami operator Δ_s and the curvatures

$$\Delta_x = \varepsilon^{-2}\partial_{zz} + \varepsilon^{-1}\kappa_0\partial_z + z\kappa_1\partial_z + \Delta_s + \varepsilon\Delta_1 + O(\varepsilon^2), \tag{2.7}$$

where κ_j is related to sums of jth powers of the curvatures

$$\kappa_i = (-1)^i\sum_{j=1}^{n-1}k_j^{i+1}, \quad \Delta_1 = -z\sum_{j=1}^{n-1}\frac{\partial k_j}{\partial s_j}\frac{\partial}{\partial s_j} + z^2\kappa_2\partial_z - 2z\kappa_0\Delta_s. \tag{2.8}$$

The Jacobian $\mathbf{J}$ of the transformation $x \mapsto (z,s)$ takes the form

$$\mathbf{J} = \Big((1+\varepsilon z k_1)\mathbf{T}^1, \dots, (1+\varepsilon z k_{n-1})\mathbf{T}^{n-1}, \varepsilon\mathbf{n}\Big) \tag{2.9}$$

and $J = |\det\mathbf{J}|$ satisfies

$$J(s,z) = \varepsilon\prod_{i=1}^{n-1}(1+\varepsilon z k_i) = \varepsilon + \varepsilon^2 z\kappa_0 + O(\varepsilon^3). \tag{2.10}$$

Definition 1. *For a function $\psi : \mathbf{R} \to \mathbf{R}$ which tends to a constant values $\psi_\infty^\pm$ at $O(1)$ exponential rates as $r \to \pm\infty$, we say that we* dress *the interface Γ with ψ, obtaining the Γ-extended function*

$$\psi_\Gamma(x) := \psi(z(x))\eta(|r(x)|/\ell) + \psi_\infty^+\big(1-\eta(r(x)/\ell)\big) + \psi_\infty^-\big(1-\eta(-r(x)/\ell\big), \tag{2.11}$$

where $\ell > 0$ is the minimal (unscaled) distance of Γ to the compliment $\mathcal{N}^c$ of its neighborhood $\mathcal{N}$ and $\eta : \mathbf{R} \to \mathbf{R}$ is a fixed, smooth cut-off function which is one on $[-\infty, 1]$ while $\eta(s) = 0$ for $s \geq 2$.

Definition 2. *Let Γ be far from self intersection. We say that $f \in L^1(\Omega)$ is localized on Γ if there exist constants $M, \nu > 0$, independent of $\varepsilon > 0$, such that*

$$|f(x(z,s))| \leq M e^{-\nu|z|}, \tag{2.12}$$

for all $x \in \Gamma_\ell$.

Lemma 2. *If Γ is far from self-intersection and f is localized on Γ, then we have the following integral formula*

$$\int_\Omega f(x)\,dx = \int_Q \int_{-\frac{\ell}{\varepsilon}}^{\frac{\ell}{\varepsilon}} f(x(z,s))J(z,s)\,dz\,ds + O\left(e^{-\nu\frac{\ell}{\varepsilon}}\right), \tag{2.13}$$

where J is the Jacobian associated to the immersion $\phi : Q = Q(t) \mapsto \Gamma(t) \subset \mathbb{R}^n$.

We assume that the initial data u_0 of (1.7) is close to a bilayer interface, that is, for some interface Γ, u_0 is close to the Γ-extension U_Γ of the homoclinic solution U of (1.5) with Lagrange multiplier $\lambda = 0$. We track the evolution of the interface $\Gamma = \Gamma(t)$ and which induces $U(t) = U_{\Gamma(t)}$. In our formal analysis we do not construct a map from U back to Γ. We record the existence of the homoclinic solution and the properties of the associated linearization in the following Lemma.

Lemma 3. *Let U be the solution of* (1.5) *which is homoclinic to b_-, corresponding to $\lambda = 0$, and even in z, then U attains it maximum value U_M at $z = 0$, where U_M is the unique zero of W in (b_-, b_+). Moreover there exists $\nu > 0$ such that the linearization,*

$$\mathcal{L} = -\partial_z^2 + W''(U), \tag{2.14}$$

operating on $H^2(\mathbf{R})$ has spectrum that satisfies

$$\sigma(\mathcal{L}) \subset \{\lambda_0, \lambda_1 = 0\} \cup [\nu, \infty). \tag{2.15}$$

where $\lambda_0 < 0$ is the ground-state eigenvalue. The corresponding eigenfunctions are $\psi_0 \geq 0$ and $\psi_1 = U_z$. Moreover we record that

$$\mathcal{L}\left(\frac{z}{2}U_z\right) = -U_{zz}, \tag{2.16}$$

$$\mathcal{L}U_{zz} = -W'''(U)U_z^2, \tag{2.17}$$

and introduce the functions $\Phi_j \in L^\infty(\mathbf{R})$ for $j = 1, 2$ which are the solutions of

$$\mathcal{L}^j \Phi_j = 1, \tag{2.18}$$

which are orthogonal to the kernel of $\mathcal{L}$.

Proof. The existence of the homoclinic solution is immediate from phase-plane considerations. Indeed writing (1.5) as a second order dynamical system in (U, U_z), there are saddle points at $(b^\pm, 0)$. Since $W(b_-) = 0 > W(b_+)$ one deduces that the unstable manifold of $(b_-, 0)$ crosses the horizontal axis at a point which we label $(U_M, 0)$. By reversibility, this orbit returns to $(b_-, 0)$ along the stable manifold, forming the homoclinic orbit. The linearization $\mathcal{L}$ is a Sturm-Liouville operator which has simple, real eigenvalues which are enumerable by their number of nodal points. Taking ∂_z of (1.5), we see that $\mathcal{L}U_z = 0$, and since U_z has one nodal point, it is the first eigenfunction, ψ_1, above the ground state ψ_0 whose eigenvalue $\lambda_0 < 0$. The remainder of the spectrum is real and an $O(1)$ distance to the right of 0. The relation (2.16) follows from a direct calculation, while (2.17) follows from taking ∂_z^2 of (1.5). The functions Φ_1 takes the form $\Phi_1 = \hat{\Phi}_1 - (W''(b_-))^{-1}$ where $\hat{\Phi}_1$ is the $L^2(\mathbf{R})$ solution to

$$\mathcal{L}\hat{\Phi}_1 = 1 - \frac{W''(U)}{W''(b_-)}. \tag{2.19}$$

Since $U \to b_-$ at an exponential rate as $z \to \infty$ the right-hand side is in L^2, and even about $z = 0$, hence orthogonal to the kernel of $\mathcal{L}$. The existence of Φ_2 follows from a similar argument. ■

We perform a multi-scale analysis of the solution u and chemical potential μ. At a time-scale τ, we have the inner spatial expansions

$$u(x,t) = \tilde{u}(s,z,\tau) = \tilde{u}_0 + \varepsilon\tilde{u}_1 + \varepsilon^2\tilde{u}_2 + \varepsilon^3\tilde{u}_3 + \dots, \tag{2.20}$$

$$\mu(x,t) = \tilde{\mu}(s,z,\tau) = \tilde{\mu}_0 + \varepsilon\tilde{\mu}_1 + \varepsilon^2\tilde{\mu}_2 + \varepsilon^3\tilde{\mu}_3 + \dots. \tag{2.21}$$

Using (2.7) we convert the Cartesian Laplacian of u into local coordinates. Collecting orders of ε we find

$$\begin{aligned}\Delta_x u =& \varepsilon^{-2}\tilde{u}_{0zz} + \varepsilon^{-1}\left(\tilde{u}_{1zz} + \kappa_0\tilde{u}_{0z}\right) + \left(\tilde{u}_{2zz} + \kappa_0\tilde{u}_{1z} + \kappa_1 z\tilde{u}_{0z} + \Delta_s\tilde{u}_0\right)\\ &+ \varepsilon\left(\tilde{u}_{3zz} + \kappa_0\tilde{u}_{2z} + \kappa_1 z\tilde{u}_{1z} + \Delta_s\tilde{u}_1 + \Delta_1\tilde{u}_0\right) + O(\varepsilon^2).\end{aligned} \tag{2.22}$$

From (1.7), we write the chemical potential $\mu = P\mathcal{A}$ where the prefactor $P := -\varepsilon^2\Delta + W''(u) - \varepsilon^2\eta_2$ acts on the Cahn-Hilliard residual $\mathcal{A} := -\varepsilon^2\Delta_x u + W'(u)$. Expanding these in turn we find

$$\begin{aligned}P =& -\partial_{zz} + W''(\tilde{u}_0) + \varepsilon\left(-\kappa_0\partial_z + W'''(\tilde{u}_0)\tilde{u}_1\right)\\ &+\varepsilon^2\left(-\kappa_1 z\partial_z - \Delta_s + W'''(\tilde{u}_0)\tilde{u}_2 + W^{(4)}(\tilde{u}_0)\frac{\tilde{u}_1^2}{2} - \eta_2\right) + (\varepsilon^3),\end{aligned} \tag{2.23}$$

$$\begin{aligned}\mathcal{A} =& \left(-\tilde{u}_{0zz} + W'(\tilde{u}_0)\right) + \varepsilon\left(-\tilde{u}_{1zz} - \kappa_0\tilde{u}_{0z} + W''(\tilde{u}_0)\tilde{u}_1\right) + \varepsilon^2\Big(-\tilde{u}_{2zz} - \kappa_0\tilde{u}_{1z}\\ &- \kappa_1 z\tilde{u}_{0z} - \Delta_s\tilde{u}_0 + W''(\tilde{u}_0)\tilde{u}_2 + \frac{1}{2}W'''(\tilde{u}_0)\tilde{u}_1^2\Big) + O(\varepsilon^3).\end{aligned} \tag{2.24}$$

Combining these expansions we group the orders of the chemical potential

$$\tilde{\mu}_0 = \left(-\partial_{zz} + W''(\tilde{u}_0)\right)\left(-\tilde{u}_{0zz} + W'(\tilde{u}_0)\right), \tag{2.25}$$

$$\begin{aligned}\tilde{\mu}_1 =& \left(-\partial_{zz} + W''(\tilde{u}_0)\right)\left(-\tilde{u}_{1zz} - \kappa_0\tilde{u}_{0z} + W''(\tilde{u}_0)\tilde{u}_1\right)\\ &+ \left(-\kappa_0\partial_z + W'''(\tilde{u}_0)\tilde{u}_1\right)\left(-\tilde{u}_{0zz} + W'(\tilde{u}_0)\right),\end{aligned} \tag{2.26}$$

$$\tilde{\mu}_2 = \Big(-\partial_{zz} + W''(\tilde{u}_0)\Big)\Big(-\tilde{u}_{2zz} + W''(\tilde{u}_0)\tilde{u}_2 - \kappa_0\tilde{u}_{1z} - \kappa_1 z\tilde{u}_{0z} + \tag{2.27}$$

$$- \Delta_s\tilde{u}_0 + \frac{1}{2}W'''(\tilde{u}_0)\tilde{u}_1^2\Big)$$

$$+\Big(-\kappa_0\partial_z + W'''(\tilde{u}_0)\tilde{u}_1\Big)\Big(-\tilde{u}_{1zz} - \kappa_0\tilde{u}_{0z} + W''(\tilde{u}_0)\tilde{u}_1\Big) +$$

$$\Big(-\kappa_1 z\partial_z - \Delta_s + W'''(\tilde{u}_0)\tilde{u}_2 + W^{(4)}\frac{\tilde{u}_1^2}{2} - \eta_2\Big)\Big(-\tilde{u}_{0zz} + W'(\tilde{u}_0)\Big). \tag{2.28}$$

Moreover we may expand the Cartesian Laplacian of the chemical potential as

$$\begin{aligned}\Delta_x\mu &= \varepsilon^{-2}\tilde{\mu}_{zz} + \varepsilon^{-1}\kappa_0\tilde{\mu}_z + z\kappa_1\tilde{\mu}_z + \Delta_s\tilde{\mu} + \varepsilon\Delta_z\tilde{\mu} + O(\varepsilon^2),\\ &= \varepsilon^{-2}\tilde{\mu}_{0zz} + \varepsilon^{-1}\left(\tilde{\mu}_{1zz} + \kappa_0\tilde{\mu}_{0z}\right) + \left(\tilde{\mu}_{2zz} + \kappa_0\tilde{\mu}_{1z} + \kappa_1 z\tilde{\mu}_{0z} + \Delta_s\tilde{\mu}_0\right)\\ &\quad + \varepsilon\left(\tilde{\mu}_{3zz} + \kappa_0\tilde{\mu}_{2z} + \kappa_1 z\tilde{\mu}_{1z} + \Delta_s\tilde{\mu}_1 + \Delta_1\tilde{\mu}_0\right) + O(\varepsilon^2).\end{aligned} \tag{2.29}$$

3. Fast times: Relaxation to the U_Γ Bi-layer

We first consider the fast-time evolution, which leads to a relaxation towards the bilayer profile for initial conditions which are sufficiently close.

(*a*) *Time scale* $T_2 = t/\varepsilon^2$ *: outer expansion*

Away from the interface, the outer expansion for the density and chemical potential takes the form

$$u(x,t) = u_0 + \varepsilon u_1 + \varepsilon^2 u_2 + \varepsilon^3 u_3 + \ldots, \tag{3.1}$$

$$\mu(x,t) = \mu_0 + \varepsilon\mu_1 + \varepsilon^2\mu_2 + \ldots, \tag{3.2}$$

where each u_i and μ_i depends upon x and $T_2 = t/\varepsilon^2$. The first two orders of the chemical potential, defined in (1.7) have the form

$$\mu_0 = W''(u_0)W'(u_0), \tag{3.3}$$

$$\mu_1 = \left(W'''(u_0)W'(u_0) + W''(u_0)^2\right)u_1. \tag{3.4}$$

For the outer expansion the time derivative $\partial_t = \varepsilon^{-2}\partial_{T_2}$ yields the expression

$$\partial_t u = \varepsilon^{-2}\partial_{T_2}u_0 + \varepsilon^{-1}\partial_{T_2}u_1 + \partial_{T_2}u_2 + \varepsilon\partial_{T_2}u_3 + \ldots, \tag{3.5}$$

while the chemical potential takes the simple form

$$\Delta\mu = \Delta\mu_0 + \varepsilon\Delta\mu_1 + \varepsilon^2\Delta\mu_2 + \ldots. \tag{3.6}$$

Applying these to the FCH equation, (1.7), and matching orders of ε, we find

$$\partial_{T_2}u_0 = 0, \quad \partial_{T_2}u_1 = 0, \quad \partial_{T_2}u_2 = \Delta\mu_0. \tag{3.7}$$

In the T_2 time scale, the outer solution u does not evolve to $O(\varepsilon^2)$.

(b) $T_2 = t/\varepsilon^2$: the inner expansion

We recall the inner expansions (2.20)-(2.21) for the concentration u and chemical potential μ, with $\tau = T_2$. We also expand the normal distance $r = r_0 + \varepsilon r_1 + O(\varepsilon^2)$, obtaining

$$\begin{aligned} u_t &= \varepsilon^{-2}\tilde{u}_{T_2} + \varepsilon^{-2}\nabla_s \tilde{u} \cdot \frac{\partial s}{\partial T_2} + \varepsilon^{-3}\frac{\partial r}{\partial T_2}\tilde{u}_z, \\ &= \varepsilon^{-3}\frac{\partial r_0}{\partial T_2}\tilde{u}_{0z} + \varepsilon^{-2}\left(\frac{\partial r_1}{\partial T_2}\tilde{u}_{0z} + \frac{\partial r_0}{\partial T_2}\tilde{u}_{1z} + \tilde{u}_{0T_2} + \nabla_s \tilde{u}_0 \cdot \frac{\partial s}{\partial T_2}\right) + O(\varepsilon^{-1}). \end{aligned} \tag{3.8}$$

Using (3.8) to expand the left-hand side of the FCH equation, (1.7), and (2.29) on the right-hand side, we find at $O(\varepsilon^{-3})$

$$\frac{\partial r_0}{\partial T_2}\tilde{u}_{0z} = 0, \tag{3.9}$$

which implies that $\partial_{T_2} r_0 = 0$ since $\tilde{u}_0$ is not constant in z. The interface $\Gamma(t)$ does not move to leading order on the T_2 time scale. At $O(\varepsilon^{-2})$ the equation (1.7) reduces to

$$\frac{\partial r_1}{\partial T_2}\tilde{u}_{0z} + \partial_{T_2}\tilde{u}_0 + \nabla_s \tilde{u}_0 \cdot \frac{\partial s}{\partial T_2} = \tilde{\mu}_{0zz}. \tag{3.10}$$

Recalling the form of $\tilde{\mu}_0$ from (2.25), and our assumption that the initial data is at leading order of the form $u_0 = U_\Gamma(x)$ where U is the homoclinic solution of (1.5) with $\lambda = 0$, which corresponds to the boundary conditions

$$\tilde{u}_0 \to b_- \quad \text{as } z \to \pm\infty, \tag{3.11}$$

it follows that $\tilde{\mu}_0 = 0$ and $u_0 = U_\Gamma$ is an equilibrium solution of (3.10). A similar analysis applies to the time scale $T_1 = t/\varepsilon$, with the conclusion that U_Γ is an equilibrium solution of (1.7) on this time scale. For brevity we omit the details.

4. The time scale t: a Gradient Flow

Applying the outer expansions (3.1) and (3.2) to (1.7) on the t time scale and collection $O(1)$ terms we obtain a nonlinear diffusion equation for u_0,

$$\partial_t u_0 = \Delta\mu_0, \quad \mu_0 = W''(u_0)W'(u_0). \tag{4.1}$$

Performing the inner expansions (2.20) and (2.21) for $\tau = t$, we have the leading order inner expressions

$$u_t = \tilde{u}_t + \nabla_s \tilde{u} \cdot \frac{\partial s}{\partial t} + \varepsilon^{-1}\frac{\partial r}{\partial t}\tilde{u}_z = \varepsilon^{-1}\frac{\partial r}{\partial t}\tilde{u}_{0z} + O(1). \tag{4.2}$$

Matching (4.2) and (2.29), the ε^{-2} and ε^{-1} terms give

$$0 = \tilde{\mu}_{0zz}, \tag{4.3}$$

$$\frac{\partial r}{\partial t}\tilde{u}_{0z} = \tilde{\mu}_{1zz} + \kappa_0\tilde{\mu}_{0z}. \tag{4.4}$$

From (4.3) it is easy to verify that $\tilde{u}_0(s,z,t)=U(z)$ is an equilibrium solution to $\tilde{\mu}_0=0$, however to derive the sharp-interface is stable within a larger framework. To this end consider a more general form for $\tilde{u}_0$,

$$\tilde{\mu}_0=\delta B_0(s,t), \tag{4.5}$$

where δ is sufficiently small, but independent of ε. A regular perturbation expansion of (2.25) about U_z shows that (4.5) leads to an inner solution

$$\tilde{u}_0(z,s,t)=U_z(z)+\delta B_0(s,t)\Phi_2(z)+O(\delta^2), \tag{4.6}$$

where $\tilde{u}_0$ is homoclinic to $b_- + \delta B_0(s,t)\alpha_-^{-2}$ along the whisker $w(s)$, and Φ_2 is defined in (2.18). Within this framework, (4.4) simplifies to

$$\frac{\partial r}{\partial t}\tilde{u}_{0z}(z)=\tilde{\mu}_{1zz}. \tag{4.7}$$

Integrating (4.7) in z from $-\infty$ to ∞, and remarking that $\frac{\partial r}{\partial t}$ is independent of z while $\tilde{u}_0$ is homoclinic in z, yields the key equalities,

$$\lim_{z\to\infty}\tilde{u}_0(z)-\lim_{z\to-\infty}\tilde{u}_0(z)=0=\lim_{z\to\infty}\tilde{\mu}_{1z}(z)-\lim_{z\to-\infty}\tilde{\mu}_{1z}(z). \tag{4.8}$$

(a) Inner-Outer Matching

The derivation of the interface evolution at this and subsequent time-scales requires a matching of the inner and the outer expansions. We follow the procedure of [Pego (1989)]. Fixing $x\in\Gamma$, we require

$$(\mu_0+\varepsilon\mu_1+\varepsilon^2\mu_2+\dots)(x+\varepsilon z\mathbf{n},t)\approx(\tilde{\mu}_0+\varepsilon\tilde{\mu}_1+\varepsilon^2\tilde{\mu}_2+\dots)(s,z,t) \tag{4.9}$$

when εz is between $O(\varepsilon)$ and $o(1)$. Expanding the left hand side around x as $\varepsilon z\to 0^+$, we have

$$\mu_0^+ +\varepsilon(\mu_1^+ + z\partial_{\mathbf{n}}\mu_0^+)+\varepsilon^2(\mu_2^+ + z\partial_{\mathbf{n}}\mu_1^+ + \frac{1}{2}z^2\partial_{\mathbf{n}}^2\mu_0^+)+\dots, \tag{4.10}$$

where $\partial_{\mathbf{n}}$ is the directional derivative along $\mathbf{n}$, and

$$\mu_i^+(x,t)=\lim_{h\to 0^+}\mu_i(x+h\mathbf{n},t) \quad \text{for all } i. \tag{4.11}$$

We can obtain a similar expansion as $\varepsilon z\to 0^-$. The matching condition (4.9) gives

$$\mu_0^\pm=\lim_{z\to\pm\infty}\tilde{\mu}_0, \tag{4.12}$$

$$\mu_1^\pm + z\partial_{\mathbf{n}}\mu_0^\pm=\tilde{\mu}_1+o(1) \quad \text{as } z\to\pm\infty, \tag{4.13}$$

$$\mu_2^\pm + z\partial_{\mathbf{n}}\mu_1^\pm + \frac{1}{2}z^2\partial_{\mathbf{n}}^2\mu_0^\pm=\tilde{\mu}_2+o(1) \quad \text{as } z\to\pm\infty, \tag{4.14}$$

$$\mu_3^\pm + z\partial_{\mathbf{n}}\mu_2^\pm + \frac{1}{2}z^2\partial_{\mathbf{n}}^2\mu_1^\pm + \frac{1}{6}z^3\partial_{\mathbf{n}}^3\mu_0^\pm=\tilde{\mu}_3+o(1) \quad \text{as } z\to\pm\infty. \tag{4.15}$$

A similar expansion yields the matching conditions for u,

$$u_0^{\pm} = \lim_{z\to\pm\infty} \tilde{u}_0, \tag{4.16}$$

$$u_1^{\pm} + z\partial_{\mathbf{n}} u_0^{\pm} = \tilde{u}_1 + o(1) \quad \text{as } z \to \pm\infty, \tag{4.17}$$

$$u_2^{\pm} + z\partial_{\mathbf{n}} u_1^{\pm} + \frac{1}{2} z^2 \partial_{\mathbf{n}}^2 u_0^{\pm} = \tilde{u}_2 + o(1) \quad \text{as } z \to \pm\infty. \tag{4.18}$$

(*b*) *Sharp interface reduction: Gradient Flow*

The matching condition (4.13) shows that $\lim_{z\to\pm\infty} \tilde{\mu}_{1z} = \partial_{\mathbf{n}} \mu_0^{\pm}$ which, in conjunction with the second equality of (4.8), implies that the normal derivative of the outer chemical potential is continuous across Γ. Similarly, the matching condition (4.16), in conjunction with the first equality of (4.8), implies the continuity of u_0. That is across the interface Γ we have the jump conditions

$$[\![\partial_{\mathbf{n}} \mu_0]\!] = [\![u_0]\!] = 0. \tag{4.19}$$

This implies that u_0 is a strong solution of (4.1) over the entire domain Ω. The evolution of the interface Γ *uncouples* from the evolution of u_0. Indeed the interface motion can be calculated after the fact. Moreover the resulting equation for u_0

$$\partial_t u_0 = \Delta \left(W''(u_0) W'(u_0) \right) \quad \text{on } \Omega, \tag{4.20}$$

subject to periodic boundary conditions, is a mass-preserving H^{-1} gradient flow on the reduced energy

$$\mathcal{F}_0(u_0) := \int_\Omega \frac{1}{2} \left(W'(u_0) \right)^2 \, dx, \tag{4.21}$$

where the effective potential $\frac{1}{2}\left(W'(u_0)\right)^2$ is a triple well with equal zeros at $b_- < b^0 < b_+$. In particular if the outer values of the initial data are sufficiently close to b_- then u_0 will converge to a constant value that is close to b_-.

For completeness of presentation, we assume the leading-order initial value $u_0(t=0)$ equals the spatial constant b_-, which is an equilibrium of (4.20), and verify that the normal velocity of the interface is indeed zero. We return to (4.7) with $\tilde{u}_0 = U_z = \hat{U}_z$, where $\hat{U} := U - b_-$, enjoys the property $\hat{U} \to 0$ as $z \to \pm\infty$. We integrate from 0 to z twice, since $\frac{\partial r}{\partial t}$ is independent of z, we obtain

$$\tilde{\mu}_1 = \tilde{\mu}_1(0) + \left(\tilde{\mu}_{1z}(0) - \frac{\partial r}{\partial t} \hat{U}(0) \right) z + \frac{\partial r}{\partial t} \int_0^z \hat{U}(\sigma) \, d\sigma. \tag{4.22}$$

We also integrate (4.7) in z from $-\infty$ to 0, which yields

$$\frac{\partial r}{\partial t} \hat{U}(0) = \tilde{\mu}_{1z}(0) - \lim_{z\to-\infty} \tilde{\mu}_{1z}(z) = \tilde{\mu}_{1z}(0) - \partial_{\mathbf{n}} \mu_0. \tag{4.23}$$

To find $\tilde{\mu}_{1z}(0)$, we simplify (2.26). Observing that $\tilde{u}_0 = U$ so that $U_{zz} - W'(U) = 0$, $-\partial_{zz} + W''(U) = \mathcal{L}$, and $\mathcal{L} U_z = 0$, we obtain

$$\tilde{\mu}_1 = \mathcal{L}^2 \tilde{u}_1. \tag{4.24}$$

From (2.15) this equation has solution $\tilde{u}_1 \in L^2(\mathbf{R})$ only if $\tilde{\mu}_1 \perp \psi_1 = U_z$. Recalling the form, (4.22), of the chemical potential $\tilde{\mu}_1$ the solvability condition reduces to

$$0 = \int_{\mathbf{R}} \left\{ \tilde{\mu}_1(0) + \left(\tilde{\mu}_{1z}(0) - \frac{\partial r}{\partial t} \hat{U}(0) \right) z + \frac{\partial r}{\partial t} \int_0^z \hat{U}(\sigma)\, d\sigma \right\} \hat{U}'\, dz, \tag{4.25}$$

and integrating by parts on $\hat{U}'$, we obtain

$$\tilde{\mu}_{1z}(0) = \frac{\partial r}{\partial t} \left\{ \int_{\mathbf{R}} \hat{U}(z)\, dz \right\}^{-1} \left\{ \hat{U}(0) \int_{\mathbf{R}} \hat{U}(z)\, dz - \int_{\mathbf{R}} \hat{U}(z)^2\, dz \right\}. \tag{4.26}$$

Combining this expression with (4.23) we obtain the normal velocity

$$V_n(s) = -\frac{\partial r}{\partial t}(s) = \frac{m}{S_1} \partial_{\mathbf{n}} \mu_0 \Big|_{\Gamma}, \tag{4.27}$$

where we have introduced the constants

$$m := \int_{\mathbf{R}} U - b_-\, dz \qquad \text{and} \qquad S_1 := \int_{\mathbf{R}} (U - b_-)^2\, dz. \tag{4.28}$$

Since $\tilde{u}_0 \equiv b_-$ on Ω, it follows that $\mu_0 \equiv 0$ on Ω and $V_n = 0$ at this time scale.

5. The time scale $t_1 = \varepsilon t$: A Quenched Mean Curvature Flow

On the time $t_1 = \varepsilon t$ we obtain the first non-trivial dynamics of the interface Γ.

(*a*) *Outer expansion*

For $t_1 = \varepsilon t$ the ∂_t derivative expands as

$$\partial_t u = \varepsilon \partial_{t_1} u_0 + \varepsilon^2 \partial_{t_1} u_1 + \varepsilon^3 \partial_{t_1} u_2 + \dots. \tag{5.1}$$

Inserting (5.1) and (3.6) in the FCH equation, (1.7), and matching terms at $O(1)$ and $O(\varepsilon)$, we have

$$0 = \Delta \mu_0, \quad \mu_0 = W''(u_0) W'(u_0), \tag{5.2}$$

$$\partial_{t_1} u_0 = \Delta \mu_1. \tag{5.3}$$

The first equation, (5.2), is consistent with our assumption that the outer-solution $u_0 = U_\Gamma = b_-$. The outer equation (5.3) reduces to

$$-\Delta \mu_1 = 0 \text{ in } \Omega_+ \cup \Omega_-, \tag{5.4}$$

where the $O(\varepsilon)$ outer chemical potential is related to the $O(\varepsilon)$ outer concentration via the expression

$$\mu_1 = \big(W'''(b_-) W'(b_-) + W''(b_-)^2 \big) u_1 = \alpha_-^2 u_1. \tag{5.5}$$

(b) Inner expansion

Recalling the inner expansion (2.20) and (2.21) at $\tau = \varepsilon t$ we expand

$$u_t = \varepsilon\left(\tilde{u}_{t_1} + \nabla_s \tilde{u} \cdot \frac{\partial s}{\partial t_1}\right) + \frac{\partial r}{\partial t_1}\tilde{u}_z = \frac{\partial r}{\partial t_1}\tilde{u}_{0z} + O(\varepsilon). \tag{5.6}$$

We insert (5.6) and (2.29) into the FCH equation and match terms at the ε^{-2}, ε^{-1} and ε^0 orders. The first equation $\tilde{\mu}_{0zz} = 0$ is consistent with our choice $\tilde{u}_0 = U$, which in fact implies $\tilde{\mu}_0 = 0$. With this reduction the remaining two equations become

$$0 = \tilde{\mu}_{1zz}, \tag{5.7}$$

$$\frac{\partial r}{\partial t_1}\tilde{u}_{0z} = \kappa_0 \tilde{\mu}_{1z} + \tilde{\mu}_{2zz} \tag{5.8}$$

The matching condition (4.13) implies that $\tilde{\mu}_{1z} \to \partial_{\mathbf{n}} \mu_0^+ = 0$ as $z \to \infty$, which, together with (5.7) implies the existence of $\tilde{B}_1(s,t)$ independent of z such that $\tilde{\mu}_1 = \tilde{B}_1$. However, since $\tilde{u}_0 = U$ the expression (2.26) for $\tilde{\mu}_1$ simplifies to

$$\tilde{B}_1 = \tilde{\mu}_1 = \mathcal{L}^2 \tilde{u}_1 \tag{5.9}$$

Recalling the function Φ_2 introduced in (2.18), we find the solution

$$\tilde{u}_1 = \tilde{B}_1(s,t)\Phi_2(s), \tag{5.10}$$

where we assumed $\tilde{u}_1 \perp \ker(\mathcal{L})$ on each whisker $w(s)$ since adding a term proportional to U_z merely serves to shift the front location. The equation (5.8) simplifies to

$$\frac{\partial r}{\partial t_1}\tilde{u}_{0z} = \tilde{\mu}_{2zz}. \tag{5.11}$$

As in Section 4, we conclude from the matching conditions that $\partial_{\mathbf{n}}\mu_1^+ = \partial_{\mathbf{n}}\mu_1^- = \partial_{\mathbf{n}}\mu_1$ while integrating (5.11) yields

$$\tilde{\mu}_2 = \tilde{\mu}_2(0) + \left(\tilde{\mu}_{2z}(0) - \frac{\partial r}{\partial t_1}\hat{U}(0)\right) z + \frac{\partial r}{\partial t_1}\int_0^z \hat{U}(\sigma)\, d\sigma, \tag{5.12}$$

and integrating (5.11) in z from $-\infty$ to 0 we obtain

$$\frac{\partial r}{\partial t_1}\hat{U}(0) = \tilde{\mu}_{2z}\Big|_{-\infty}^{0} = \tilde{\mu}_{2z}(0) - \partial_{\mathbf{n}}\mu_1^-. \tag{5.13}$$

To calculate $\tilde{\mu}_{2z}(0)$, we return to (2.28), and recall that $\tilde{u}_0 = U$ while from (5.10), we deduce that $\mathcal{L}\tilde{u}_1 = \tilde{B}_1\Phi_1$. With these simplifications we have

$$\begin{aligned}\tilde{\mu}_2 = \mathcal{L}&\left(-\tilde{u}_{2zz} - \kappa_0\tilde{u}_{1z} - \kappa_1 z U_z + W''(U)\tilde{u}_2 + \frac{1}{2}W'''(U)\tilde{u}_1^2\right)\\ &+ \left(-\kappa_0\partial_z + W'''(U)\tilde{B}_1\Phi_2\right)\left(\tilde{B}_1\Phi_1 - \kappa_0 U_z\right).\end{aligned} \tag{5.14}$$

We may solve for $\tilde{u}_2$ if and only if we can invert $\mathcal{L}^2$, which requires

$$\tilde{\mu}_2 - \left(-\kappa_0\partial_z + W'''(U)\tilde{B}_1\Phi_2\right)\left(\tilde{B}_1\Phi_1 - \kappa_0 U_z\right) \perp U_z. \tag{5.15}$$

From parity considerations the non-zero terms in the integral are

$$\int_{\mathbf{R}} \left(\tilde{\mu}_2 + \tilde{B}_1\kappa_0(\Phi_1' + W'''(U)\Phi_2 U')\right) U'\, dz = 0.$$

However using (2.17) we rewrite the last term above as

$$\int_{\mathbf{R}} W'''(U)(U')^2\Phi_2\, dz = -\int_{\mathbf{R}} \Phi_2 \mathcal{L} U''\, dz = -\int_{\mathbf{R}} U''\Phi_1\, dz, \tag{5.16}$$

so that it combines with the middle term. Moreover, using (2.16) we find,

$$-\int_{\mathbf{R}} 2U''\Phi_1\, dz = \int_{\mathbf{R}} \mathcal{L}(z\hat{U}_z)\Phi_1\, dz = \int_{\mathbf{R}} z\hat{U}'\, dz = -\int_{\mathbf{R}} \hat{U}\, dz. \tag{5.17}$$

Substituting for $\tilde{\mu}_2$ from (5.12) and (5.13), we reduce the solvability condition to

$$\int_{\mathbf{R}} \left(\partial_{\mathbf{n}}\mu_1^- z + \frac{\partial r}{\partial t_1}\int_0^z \hat{U}(\sigma)\, d\sigma\right)\hat{U}_z\, dz = \tilde{B}_1\kappa_0 \int_{\mathbf{R}} \hat{U}\, dz. \tag{5.18}$$

Integrating by parts and solving for the normal velocity we obtain

$$V_n = -\frac{\partial r}{\partial t_1} = \frac{m}{S_1}\left(\partial_{\mathbf{n}}\mu_1^- + \tilde{B}_1\kappa_0\right), \tag{5.19}$$

where we recall the constants m and S_1 from (4.28).

(c) Sharp interface limit: Quenched curvature driven flow

We summarize the $t_1 = \varepsilon t$ evolution in the following model,

$$\Delta\mu_1 = 0 \qquad \text{in } \Omega\setminus\Gamma, \tag{5.20}$$

$$[\![u]\!] = [\![\partial_{\mathbf{n}}\mu_1]\!] = 0 \qquad \text{on } \Gamma, \tag{5.21}$$

$$V = \frac{m}{S_1}\left(\partial_{\mathbf{n}}\mu_1 + \tilde{B}_1\kappa_0\right) \qquad \text{on } \Gamma. \tag{5.22}$$

Indeed, (5.20)-(5.21) imply that $\Delta\mu_1 = 0$ in Ω, and with periodic boundary conditions on $\partial\Omega$, it follows from the maximum principle that μ_1 is a spatial constant $\mu_1(x,t) = B_1(t_1)$ for all $x \in \Omega$. Consequently $\partial_{\mathbf{n}}\mu_1 = 0$ on Γ, and by continuity of the inner and outer chemical potentials, we have $\tilde{\mu}_1 = \tilde{B}_1(s,t_1) = B_1(t_1)$, and the motion of the interface on the t_1 time scale reduces to

$$V = \frac{m}{S_1}B_1(t_1)\kappa_0. \tag{5.23}$$

The value of B_1 is related to u_1 through (5.5), and is determined in part via the conservation of the total mass of the minority phase,

$$M := \int_\Omega u(x,t) - b_-\, dx = \int_\Omega u(x,0) - b_-\, dx, \tag{5.24}$$

which is fixed by the initial data. This value couples to the flow, (5.23); if the evolution causes the interface Γ to lengthen, then either its width must compress or minority phase must be drawn from the outer region, lowering the value of u_1.

In the outer region $\Omega\backslash\Gamma_\ell$ we have the expansion

$$u = b_- + \varepsilon\frac{B_1}{\alpha_-^2} + O(\varepsilon^2), \tag{5.25}$$

while in the inner region, Γ_ℓ from (5.10) the inner expansion takes the form

$$u = U(z) + \varepsilon B_1(t_1)\Phi_2(z) + O(\varepsilon^2). \tag{5.26}$$

We insert these expansions into the right-hand side of (5.24)

$$M = \int_{\Omega\backslash\Gamma_\ell} \varepsilon\frac{B_1}{\alpha_-^2}\,dx + \int_{\Gamma_\ell} \hat{U}(z) + \varepsilon B_1\Phi_2(z)\,dx + O(\varepsilon^2). \tag{5.27}$$

Assuming that $|\Gamma| = O(1)$, changing to whiskered coordinates in the localized integrals, and using the Jacobian expansion (2.10), we find at leading order

$$M = \varepsilon\left(|\Omega|\frac{B_1}{\alpha_-^2} + \int_Q\int_{-\ell/\varepsilon}^{\ell/\varepsilon} \hat{U}(z)\,dzds\right) + O(\varepsilon^2). \tag{5.28}$$

We expand $M = M_1\varepsilon + M_2\varepsilon^2 + O(\varepsilon^2)$ and the surface area $|\Gamma| = \gamma_0 + \varepsilon\gamma_1 + O(\varepsilon^2)$, evaluate the integrals, and recall the definition of m from (4.28), to obtain

$$M_1 = \left(|\Omega|\frac{B_1}{\alpha_-^2} + \gamma_0 m\right). \tag{5.29}$$

This permits us to solve for B_1 in terms of the length of the interface,

$$B_1 = \frac{\alpha_-^2}{|\Omega|}(M_1 - \gamma_0 m) < 0, \tag{5.30}$$

where the negativity of B_1 is a condition imposed on the initial data, see the discussion following (1.8). On the other hand, when subject to a normal velocity V, measured in time units t_1, the interfacial surface area grows at the rate

$$\frac{d|\Gamma|}{dt_1} = \int_\Gamma \kappa_0(s)V(s)\,ds, \tag{5.31}$$

so that, the interfaces, $\Gamma(t)$ subject to (5.23) have the leading order growth

$$\frac{d}{dt_1}\gamma_0(t_1) = \frac{m}{S_1}B_1\int_\Gamma \kappa_0^2(s)\,ds. \tag{5.32}$$

Taking ∂_{t_1} of (5.30) we arrive at the ordinary differential equation

$$\frac{d}{dt_1}B_1 = -\frac{m^2\alpha_-^2}{|\Omega|S_1}B_1\int_\Gamma \kappa_0^2(s)\,ds. \tag{5.33}$$

In particular, B_1, and hence μ_1 and u_1 decay exponentially to zero on the t_1 time scale. Naturally, the total mass M_1, given in (5.29), is conserved under the flow, so the equilibrium interfacial length satisfies $\gamma_0^* = \frac{M_1}{m}$. While it is possible that portions of the interface Γ become singular in finite time, that is Γ may fail to be far from self-intersection, generically one expects the interface to move an $O(1)$ amount in an $O(\varepsilon^{-1})$ time, as measured in the unscaled x and t, before approaching its t_1 equilibrium.

For the particular case in which Γ is comprised of N disjoint, hollow balls (i.e. spherical vesicles) of radii $R_i = R_i(t_1)$, in $\Omega \subset \mathbf{R}^n$, the quenched-curvature driven flow reduces to

$$\frac{d}{dt_1} R_i = \frac{m(n-1)}{S_1} \frac{B_1}{R_i}, \quad \text{for} \quad i = 1, \cdots, N, \tag{5.34}$$

$$\frac{d}{dt_1} B_1 = -\frac{m^2 \alpha_-^2 \alpha_n (n-1)^2}{|\Omega| S_1} B_1 \sum_{i=1}^{N} R_i^{n-3}, \tag{5.35}$$

where α_n is the surface area of the unit ball in $\mathbf{R}^n$. The conserved quantity takes the form

$$M_1 = \frac{|\Omega|}{\alpha_-^2} B_1 + m\alpha_n \sum_{i=1}^{N} R_i^{n-1}. \tag{5.36}$$

If $B_1(0) > 0$ then each ball grows in radius to a finite limit. If $B_1(0) < 0$ then it is possible individual balls may collapse to an $O(\varepsilon)$ radius before B_1 tends to zero, in which case the evolution (5.34)-(5.35) breaks down.

6. The time scale $t_2 = \varepsilon^2 t$: surface-area preserving Willmore flow

For the $t_2 = \varepsilon^2 t$ time scale, the outer solution has equilibrated to $u_0 = b_-$ and $u_1 = 0$. As a consequence the outer expansion reduces to

$$u = b_- + \varepsilon^2 u_2 + \varepsilon^3 u_3 + \dots, \tag{6.1}$$

$$\mu = \varepsilon^2 \mu_2 + \varepsilon^3 \mu_3 + \dots. \tag{6.2}$$

Matching terms in (1.7) in the outer region yields

$$\Delta \mu_2 = 0. \tag{6.3}$$

The inner expansion reduces to

$$u(x,t) = \tilde{u}(s,z,t) = U_\Gamma + \varepsilon^2 \tilde{u}_2 + \varepsilon^3 \tilde{u}_3 + \dots, \tag{6.4}$$

$$\mu(x,t) = \tilde{\mu}(s,z,t) = \varepsilon^2 \tilde{\mu}_2 + \varepsilon^3 \tilde{\mu}_3 + \dots, \tag{6.5}$$

so that the left-hand side of (1.7) take the form

$$u_t = \varepsilon^2 \left(\tilde{u}_{t_2} + \nabla_s \tilde{u} \cdot \frac{\partial s}{\partial t_2} \right) + \varepsilon \frac{\partial r}{\partial t_2} \tilde{u}_z = \varepsilon \frac{\partial r}{\partial t_2} \tilde{u}_{0z} + O(\varepsilon^2). \tag{6.6}$$

Inserting (6.6) and (2.29) in (1.7), the ε^{-2} and ε^{-1} terms give

$$0 = \tilde{\mu}_{2zz} \tag{6.7}$$

$$\frac{\partial r}{\partial t_2} U' = \kappa_0 \tilde{\mu}_{2z} + \tilde{\mu}_{3zz}. \tag{6.8}$$

The equation (6.7) and matching condition (4.14) implies the existence of $B_2(s,t)$, independent of z, such that $\tilde{\mu}_2 = B_2$. In light of (6.4) we expand (2.28), to find

$$B_2 = \tilde{\mu}_2 = \mathcal{L}^2 \tilde{u}_2 + (2\kappa_1 + \kappa_0^2) U''. \tag{6.9}$$

Since both U'' and B_2 are orthogonal to the kernel of $\mathcal{L}$ we can solve for $\tilde{u}_2$,

$$\tilde{u}_2 = B_2 \Phi_2 - (2\kappa_1 + \kappa_0^2)\Psi_2, \tag{6.10}$$

where Φ_2 was introduced in (2.18) while $\Psi_j \perp U_z$ satisfies $\mathcal{L}^j \Psi_j = U''$.

Turning to equation (6.8), it simplifies to

$$\frac{\partial r}{\partial t_2} U' = \tilde{\mu}_{3zz}. \tag{6.11}$$

As in Section 4, we can conclude that $\partial_{\mathbf{n}} \mu_2^+ = \partial_{\mathbf{n}} \mu_2^- = \partial_{\mathbf{n}} \mu_2$, so that the outer chemical potential μ_2 will solve (6.3) in all of Ω, in particular it is constant.

To derive the motion of the interface we return to (6.11) and integrate twice from 0 to z, which yields,

$$\tilde{\mu}_3 = \tilde{\mu}_3(0) + \left(\tilde{\mu}_{3z}(0) - \frac{\partial r}{\partial t_2} \hat{U}(0) \right) z + \frac{\partial r}{\partial t_2} \int_0^z \hat{U}(\sigma)\, d\sigma, \tag{6.12}$$

while integrating from z from $-\infty$ to 0, are recalling that $\tilde{\mu}_2$ is constant yields

$$\frac{\partial r}{\partial t_2} \hat{U}(0) = \tilde{\mu}_{3z} \Big|_{-\infty}^{0} = \tilde{\mu}_{3z}(0) - \partial_{\mathbf{n}} \mu_2 = \tilde{\mu}_{3z}(0), \tag{6.13}$$

To evaluate $\tilde{\mu}_{3z}(0)$ we need the $O(\varepsilon^3)$ terms in the inner expansion of $P\mathcal{A}$ from (2.23) and (2.24). In general this is cumbersome, but since $\tilde{u}_0 = U$ and $\tilde{u}_1 = 0$, we simplify the expression for P and $\mathcal{A}$ and derive the inner chemical potential

$$\begin{aligned} \tilde{\mu}_3 = \mathcal{L}\Big(\mathcal{L}\tilde{u}_3 - \kappa_0 \tilde{u}_{2z} - \kappa_2 z^2 \tilde{u}_{0z} \Big) - \kappa_0 \partial_z \Big(\mathcal{L}\tilde{u}_2 - \kappa_1 z \tilde{u}_{0z} \Big) \\ + \Big(-\kappa_1 z \partial_z + W'''(\tilde{u}_0)\tilde{u}_2 - \Delta_s - \eta_2 \Big)(-\kappa_0 \tilde{u}_{0z}). \end{aligned} \tag{6.14}$$

Using the relation (6.10) for $\tilde{u}_2$ we re-write this in the form

$$\mathcal{L}\Big(\mathcal{L}\tilde{u}_3 - \kappa_0 \tilde{u}_{2z} - \kappa_2 z^2 \tilde{u}_{0z} \Big) = R_2, \tag{6.15}$$

where we have introduced the t_2 residual

$$\begin{aligned} R_2 := \tilde{\mu}_3 + \kappa_0 B_2 \left(\Phi_1' + W'''(U)\Phi_2 U' \right) - (2\kappa_1 + \kappa_0^2)\kappa_0 \left(\Psi_1' + W'''(U)\Psi_2 U' \right) + \\ - \kappa_0 \kappa_1 \Big(U' + 2zU'' \Big) - (\Delta_s + \eta_2)\kappa_0 U'. \end{aligned} \tag{6.16}$$

The solvability condition requires that $R_2 \perp_{L^2(\mathbf{R})} U'$. We examine the terms one by one. First , from (6.12) and (6.13), we have

$$\int_{\mathbf{R}} \tilde{\mu}_3 U'\, dz = -m\tilde{\mu}_{3z}(0) + \frac{\partial r}{\partial t_2}(\hat{U}(0)m - S_1) = -S_1 \frac{\partial r}{\partial t_2}. \tag{6.17}$$

For the next two terms, since $\mathcal{L}$ is self-adjoint, using (2.17) and (2.16), we find

$$\int_{\mathbf{R}} (\Phi_1' + W'''(U)\Phi_2 U')U'\,dz = -2\int_{\mathbf{R}} U''\Phi_1\,dz = \int_{\mathbf{R}} \mathcal{L}(zU')\Phi_1\,dz = -m, \quad (6.18)$$

$$\int_{\mathbf{R}} (\Psi_1' + W'''(U)\Psi_2 U')U'\,dz = \int_{\mathbf{R}} \mathcal{L}(zU')\Psi_1\,dz = \int_{\mathbf{R}} zU'U''\,dz = -\frac{1}{2}S_2, \quad (6.19)$$

where m is defined in (4.28) and we have introduced

$$S_2 := \int_{\mathbf{R}} (U')^2\,dz. \quad (6.20)$$

The fourth term yields no contribution,

$$\int_{\mathbf{R}} (U' + 2zU'')U'\,dz = 0. \quad (6.21)$$

Inserting these results into the solvability condition, and isolating the normal velocity, we find

$$V_n = -\frac{\partial r}{\partial t_2} = \frac{S_2}{S_1}\left(\Delta_s + \eta_2 + \frac{m}{S_2}B_2 - \left(\kappa_1 + \frac{\kappa_0^2}{2}\right)\right)\kappa_0. \quad (6.22)$$

(a) The mass constraint

As was the case for the t_1 time scale, the value $B_2 = B_2(t_2)$ of the outer chemical potential, μ_2, is determined by the conservation of total mass of the minority phase, whose integral we break over the inner and outer regions

$$M := \int_{\Omega} u(x,t) - b_-\,dx = \int_{\Omega\backslash\Gamma_\ell} (u - b_-)\,dx + \int_{\Gamma_\ell} (\tilde{u} - b_-)\,dx. \quad (6.23)$$

In the outer region, the solution takes the form (3.1) with $u_0 = b_-$, $u_1 = 0$, and $B_2 = \mu_2 = [W''(u_0)]^2 u_2 = \alpha_-^2 u_2$. In particular $u_2 = B_2\alpha_-^{-2}$ is a spatial constant. Since $|\Gamma| = O(1)$, the outer integral reduces to

$$\int_{\Omega\backslash\Gamma_\ell} (u - b_-)\,dx = \int_{\Omega\backslash\Gamma_\ell} (\varepsilon^2 u_2 + O(\varepsilon^3))\,dx = \varepsilon^2\frac{B_2|\Omega|}{\alpha_-^2} + O(\varepsilon^3). \quad (6.24)$$

In the inner domain u has an expansion (2.20) with $\tilde{u}_0 = U(z)$, $\tilde{u}_1 = 0$. Using (2.13) to change to the whiskered coordinates and expanding the Jacobian from (2.10), the inner integral reduces to

$$\begin{aligned}\int_{\Gamma_\ell} (\tilde{u} - b_-)dx &= \int_{\Gamma}\int_{|z|\le\ell/\varepsilon} (\tilde{u} - b_-)J(s,z)\,dzds, \quad (6.25)\\ &= \int_{\Gamma}\int_{|z|\le\ell/\varepsilon} \hat{U}(z)(\varepsilon + \varepsilon^2 z\kappa_0)\,dzds + O(\varepsilon^3) = \varepsilon m|\Gamma| + O(\varepsilon^3).\end{aligned}$$

Combining the outer, (6.24), and inner, (6.25), integrals, we find the balance

$$M = \varepsilon m|\Gamma| + \varepsilon^2 B_2\alpha^{-2}|\Omega| + O(\varepsilon^3). \quad (6.26)$$

Scaling the minority mass as $M=\varepsilon M_1$ and expanding the interfacial surface area as $|\Gamma|=\gamma_0+\varepsilon\gamma_1+\cdots$, we find that at leading order all the minority phase is located on the interface, whose surface area is fixed over the t_2 evolution

$$\gamma_0=m^{-1}M_1. \tag{6.27}$$

At second order, we obtain an expression for the outer chemical potential

$$B_2=-m\gamma_1\frac{\alpha_-^2}{|\Omega|}. \tag{6.28}$$

Recalling the relation (5.31), we have

$$\int_\Gamma \kappa_0(s)V_n(s)\,ds=\frac{d|\Gamma|}{dt_2}=\varepsilon\frac{d\gamma_1}{dt_2}+O(\varepsilon^2)=O(\varepsilon). \tag{6.29}$$

In particular, since the interface surface area is conserved to leading order, this forces the value of B_2,

$$B_2=-\frac{S_2}{m}\frac{\int_\Gamma -|\nabla_s\kappa_0|^2+\eta_2\kappa_0^2-(\kappa_1+\frac{1}{2}\kappa_0^2)\kappa_0^2\,ds}{\int_\Gamma \kappa_0^2\,ds}. \tag{6.30}$$

We may express the normal velocity more succinctly by introducing the zero-average, mean-curvature-weighted projection associated to the interface Γ,

$$\Pi_\Gamma[f]:=f-\kappa_0\frac{\int_\Gamma f(s)\kappa_0(s)\,ds}{\int_\Gamma \kappa_0^2(s)\,ds}, \tag{6.31}$$

which maps $L^1(\Gamma)$ into itself with the property that the normal velocity $\Pi_\Gamma V$ preserves surface area. The leading order evolution of the interface Γ, at the t_2 time scale can be written as

$$V_n=\frac{S_2}{S_1}\Pi_\Gamma\left[\left(\Delta_s-\left(\kappa_1+\frac{\kappa_0^2}{2}\right)\right)\kappa_0\right], \tag{6.32}$$

where the constant η_2 drops out since $\Pi_\Gamma[\eta_2\kappa_0]=0$.

(*b*) *Evolution of disjoint spherical vesicles*

As in section 5, consider an initial configuration of N well-separated vesicles of radii $R_i=R_i(t_2)$ contained in a periodic domain $\Omega\subset\mathbf{R}^n$. In $\mathbf{R}^n$, on the i'th sphere each curvature $k_j=R_i^{-1}$, for $j=1,\cdots,n-1$, which yields the relations $\kappa_0=(n-1)R_i^{-1}$ and $\kappa_1=-(n-1)R_i^{-2}$. The normal velocity, (6.32), can be written as

$$\frac{dR_i}{dt_2}=-\frac{(n-1)^2(n-3)S_2}{2S_1}\Pi_\Gamma\left[R^{-3}(s)\right], \tag{6.33}$$

where $R(s):=R_i$ for s on the i'th sphere. The integrals in the projection take the value

$$\frac{\int_\Gamma R^{-3}(s)\kappa_0(s)\,ds}{\int_\Gamma \kappa_0^2(s)\,ds}=\frac{1}{n-1}\frac{\sum_{j=1}^{n-1}R_j^{n-5}}{\sum_{j=1}^{n-1}R_j^{n-3}}=:\frac{1}{R_c^2}, \tag{6.34}$$

where $R_c = R_c(t_2)$ defines a critical radius that varies in time. So the evolution reduces to

$$\frac{dR_i}{dt} = -\frac{(n-1)^2(n-3)S_2}{2S_1}\frac{1}{R_i}\left[\frac{1}{R_i^2} - \frac{1}{R_c^2}\right]. \tag{6.35}$$

In space dimension $n=2$, the coefficient is positive and one can verify that balls with radii bigger than R_c shrink, while those with radii smaller than R_c grow. In space dimension $n=3$ the coefficient is zero and the radii do not change on the t_2 time scale. For $n \geq 4$, balls with radii larger than R_c grow, while those with radii smaller than R_c shrink and disappear in finite time, leading to a coarsening phenomenon and eventually a winner-take all scenario, assuming the stability of the underlying structures.

7. Conclusion

The Functionalized Cahn-Hilliard equation supports different classes of interfaces than the Cahn-Hilliard equation, and these interfaces manifest significantly different dynamics, in particular collections of closed bilayers evolve on long time scales according to a surface area preserving Willmore flow. More specifically the long-range interaction between single-layer interfaces in the Cahn-Hilliard equation is mediated through a Mullins-Sekerka problem. For the FCH gradient flow the long-range interaction is mediated through the spatially constant outer chemical potential – its value below equilibrium dictates the growth or decay of each bilayer.

There are many possible areas to investigate, both in model development and model analysis. It is quite intriguing to consider extensions beyond binary mixtures, indeed a preliminary discussion in this direction can be found in [Gavish et al (2012)]. For example, bilayers need not only form a barrier between the same phase, but can also separate two distinct phases. This requires a three-phase model, one for the surfactant which forms the separating membrane, and two for the distinct separated phases. The bilayer structure is still required to incorporate the competition for a scarce membrane/surfactant phase; moreover such a 'third-phase' membrane can rupture, resulting in mixing of the two bulk phases, as well as support mergings between distinct membrane structures.

The most challenging issues are the competition between the wide variety of possible stable morphologies supported by the FCH gradient flows. In on-going work, [Dai and Promislow (2013)], the authors have extended the analysis presented here to incorporate a co-dimension two, or closed cylindrical pore structures. As in the situation investigated in this work, the competition between between co-exisiting bilayers and pores for scarce surfactant phase is mediated through the constant value of the outer chemical potential, this competition is quite evocative of the "phospholipid war" proposed in [Budin & Szostak (2011)] as a fundamental evolutionary force in early cell membranes. However this analysis avoids the central issue: the role of tremendous number of locally stable "defect structures" supported by the FCH free energy. These are the end-caps of open pores and the rims of open bilayers – called bicelles in the biological literature, [Shinoda et al (2011)]. Indeed, it is tempting to conjecture that the FCH model will provide a more accurate estimation of the free energy of highly curved interfaces than the usual Cahn-Hilliard free energy, which is known to significantly underestimate this energy, [Du et al (2004), **?**]. This presumption arises from the fact that for co-dimension one interfaces the squared variational derivative term in the FCH energy naturally yields a contribution proportional to $\int_\Gamma \varepsilon^2 H^2 \, dS$, where H is the mean curvature of the co-dimension one interface Γ. However for a strongly curved interface the coordinate system presented in Lemma 1 becomes singular when $H \sim \varepsilon^{-1}$ at which point the bilayer structure is likely to degenerate, quite likely resulting in the generation of a defect structure. The mathematical characterization of these defect structures, their role in mergings and bifurcations, and their impact on competitive geometric evolution and Γ-limits awaits those with the requisite curiosity.

Acknowledgement: K. P. acknowledges support from the National Science Foundation under grants DMS 0708804, DMS 093468, and DMS 1125231. This work was completed while S. D. was funded under DMS 093468.

References

Budin, I. and Szostak, J. 2011, Physical effects underlying the transition from primative to modern cell membranes, *Proc. Natl. Acad. Sci. USA*, 108:5249-5254.

Cahn, J.W. and Hilliard, J.E. 1958, Free energy of a nonuniform system. I. Interfacial energy, *J. Chem. Phys.*, 28:258-267.

Cahn, J. W., Elliott, C. M. & Novick-Cohen, A. 1996 The Cahn-Hilliard equation with a concentration-dependent mobility: motion by minus the Laplacian of the mean curvature, *European J. Appl. Math.*, 7:287–301.

Canham, P. 1970 Minimum energy of bending as a possible explanation of biconcave shape of human red blood cell, *J. Theor. Biol.* 26:61–81.

Dai, S. and Du, Q. 2012 Motion of interfaces governed by the Cahn-Hilliard equation with highly disparate diffusion mobility, *SIAM J. Appl. Math.* 72(6): 1818-1841.

Dai, S. and Promislow, K. 2013 Competitive geometric evolution of surfactant wetted interfacial structures, *submitted.*

Doelman, A. and Promislow, K. 2012, Equlibria of the Functionalized Cahn-Hilliard energy: Stability and Competition, *preprint.*

Du, Q., Liu, C., and Wang, X. 2004, A phase field approach in the numerical study of the elastic bending energy for vesicle membranes *J. Comp. Physics* 198:450-468.

Du, Q., Liu, C., and Wang, X. 2006, Simulating the deformation of vesicle membranes under elastic bending energy in three dimensions, *J. Comp. Physics* 212:757-777.

Gavish, N., Hayrapetyan, G., Promislow, K. & Yang, L. 2011 Curvature driven flow of bilayer interfaces, *Physica D*, 240:675–693.

Gavish, N., Jones, J., Xu, Z. , Christlieb, A., Promislow, K. 2012, Variational Models of Network Formation and Ion Transport: Applications to Perfluorosulfonate Ionomer Membranes, *Polymers*, 4:630–655.

Gompper, G. and Schick, M. 1990, Correlation between Structural and Interfacial Properties of Amphiphilic Systems, *Phys. Rev. Lett.* 65:1116-1119.

Helfrich, W. 1973 Elastic properties of lipid bilayers - theory and possible experiments, *Zeitshcrift fur naturforschung C* 28:693–703.

Loreti, P. and March, R. 2000, Propagation of fronts in a nonlinear fourth order equation, *Euro. Jnl. of Applied Mathematics* 11:203-213.

Lowengrub, J., Ratz, A., and Voigt, A. 2009, Phase-field modeling of the dynamics of multicomponent vesicles: Spinodal decomposition, coarsening, budding, and fission, *Phy. Rev. E* 79:031925-1:13.

Modica, L. 1987 The gradient theory of phase transitions and the minimal interface criterion, *Arch. Rational. Mech. Anal.* 98:123-142.

Pego, R. L. 1989 Front migration in the nonlinear Cahn-Hilliard equation. *Proc. Royal Soc. London A*, 442:261–278.

Promislow, K., Wetton, B. 2009 PEM fuel cells: A mathematical overview, *SIAM Journal on Applied Mathematics*, 70:369-409.

Röger, M. and Schätzle, R. 2006, On a modified conjecture of De Giorgi, *Math. Z.* 254:675-714.

Sinoda, W., Nakamura, T., and Nielsen, S. 2011, Free energy analysis of vesicle-to-bicelle transformation, *Soft Matter* 7:9012.

Sternberg, P. 1988, The effect of a singular perturbation on nonconvex variational problems, *Arch. Rational Mech. Anal.* 101:209-260.

Torabi, S., Lowengrub, J., Voigt, A., and Wise, S. 2009 A new phase-field model for strongly aniostropic systems, *Proc. Royal Society A* 465:1337-1359.

Wang, X. and Du, Q. 2008, Modelling and Simulations of Multi-component Lipid Membranes and Open Membranes via Diffuse Interface Approaches, *J. Math. Bio.* 56(3):347-371.

Wise, S. M., Kim, J., and Lowengrub, J. S. 2007, Solving the regularized, strongly anisotropic CahnÐ Hilliard equation by an adaptive non-linear multigrid method. *J. Comp. Phys.* 226:414-446.

Zhu, T.F., Adamala, K., Zhang, N., and Szostak, J. W. 2012 Photochemically driven redox chemistry induces protocell membrane pearling and division, *Proc. Natl. Acad. Sci. USA* 109: 9828-9832.