CHAPTER 4

The Cahn–Hilliard Equation

Amy Novick-Cohen
Technion-IIT, *Haifa* 32000, *Israel*

Contents

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1. Introduction

The present chapter is devoted to the Cahn–Hilliard equation [16,15]:

$$u_t = \nabla \cdot M(u)\nabla\big[f(u) - \epsilon^2 \Delta u\big], \quad (x,t) \in \Omega \times \mathbb{R}^+, \tag{1}$$

$$n \cdot \nabla u = n \cdot M(u)\nabla\big[f(u) - \epsilon^2 \Delta u\big] = 0, \quad (x,t) \in \partial\Omega \times \mathbb{R}^+, \tag{2}$$

$$u(x,0) = u_0(x), \quad x \in \Omega. \tag{3}$$

Here $0 < \epsilon^2 \ll 1$ is a "coefficient of gradient energy", $M = M(u)$ is a "mobility" coefficient, and $f = f(u)$ is a "homogeneous free energy". The equation was initially developed to describe phase separation is a two component system, with $u = u(x,t)$ representing the *concentration* of one of the two components. Typically, the domain Ω is assumed to be a bounded domain with a "sufficiently smooth" boundary, $\partial\Omega$, with n in (2) representing the unit exterior normal to $\partial\Omega$. It is reasonable to consider evolution for times $t > 0$, or on some finite time interval $0 < t < T < \infty$.

Concentration should be understood as referring either to *volume fraction* or to *mass fraction*, depending on the physical system under investigation. By *volume fraction* we mean the volume fraction per unit volume of say component "A", in a system containing two components which we shall denote by "A" and "B". The meaning of *mass fraction* is analogous. Thus the Cahn–Hilliard equation constitutes a continuous, as opposed to a discrete or lattice description, of the material undergoing phase separation. Such a description is appropriate under many but not all circumstances. Note that the definition of $u(x,t)$ implies that $u(x,t)$ should satisfy $0 \leqslant u(x,t) \leqslant 1$. Moreover, if $u(x,t)$, the concentration of component A, is known, then the concentration of the second component is given by $1-u$ and is hence also known; thus the evolution of the composition of the two component system is being predicted by a single scalar Cahn–Hilliard equation.

In the context of the Cahn–Hilliard equation, the two components could refer, for example, to a system with two metallic components, or two polymer components, or say, two glassy components. Frequently in materials science literature, concentration is given in terms of *mole fraction* or equivalently *number fraction*, rather than in terms of volume fraction or mass fraction. A mole refers to 6.02252×10^{23} molecules (Avogadro's number of molecules), and the mole fraction of component A refers to the number of A molecules per mole of the two component system, locally evaluated. Mole fraction of number fraction are equivalent to volume fraction if the molar volume (the volume occupied by one mole) is independent of composition, which is rarely strictly correct [15]. For example, in a two component polymer systems when many of the polymers are long, the configuration of the polymers, i.e. whether they are "stretched out" or "rolled up", typically depends on composition, which in turn influences the molar volume. Notice also that often temperature does not appear explicitly in the Cahn–Hilliard equation, since the model is based on the assumption that the temperature is constant; such an assumption requires careful temperature control and is also rarely strictly fulfilled in reality. The model also assumes *isotropy* of the system, which can also only be approximately correct for metallic systems [5,77, 87], for which the equations were designed, which have an inherent crystalline structure unless they are in a liquid phase. Nevertheless, the Cahn–Hilliard equation has been seen to contain many of the dominant *paradigms* for phase separation dynamics, and as such, has

played, and continues to play, an important role in understanding the evolution of phase separation.

Why does the Cahn–Hilliard equation appear in so many different contexts, and what behavior is predicted by the Cahn–Hilliard equation which is common to all these systems? Off-hand, what is being modeled with the Cahn–Hilliard equation is phase separation, in other words, the segregation of the system into spatial domains predominated by one of the components, in the presence of a mass constraint, and what one wishes to accomplish here is to model the dynamics in a sufficiently accurate fashion so that many of the various features of the resultant pattern formation evolution that one sees in nature during phase separation can be explained and predicted. In materials science this pattern formation is referred to as the *microstructure* of the material, and the microstructure is highly influential in determining many of the properties of the material, such as strength, hardness, and conductivity. The Cahn–Hilliard model is rather broad ranged in its evolutionary scope; it can serve as a good model for many systems during early times, it can give a reasonable qualitative description for these systems during intermediary times, and it can serve as a good model for even more systems at late times. Often, the late time evolution is so slow that the pattern formation or microstructure becomes effectively frozen into the system over time scales of interest, and hence it is the long time behavior of the system which is seen in practice.

The Cahn–Hilliard equation also appears in modeling many other phenomena. These include the evolution of two components of intergalactic material [80], the dynamics of two populations [19], the biomathematical modeling of a bacterial film [46], and certain thin film problems [69,79]. We apologies to the reader that most of the details pertaining to the modeling of these phenomena are outside the scope of the present survey. Nevertheless, we invite the interested reader to have a look at the forthcoming book by the author of this survey, entitled *From Backwards Diffusion to Surface Diffusion: the Cahn–Hilliard Equation* [65], where these and other details will be treated in greater depth.

We hope that this survey will clarify for the reader the notions of backwards diffusion and surface diffusion and their connection with the Cahn–Hilliard equation, and will convey something of the nature of the physical phenomena which accompany phase separation and how the Cahn–Hilliard equation manages to capture these features.

2. Backwards diffusion and regularization

Let us consider a simple variant of the Cahn–Hilliard equation in which $f(u) = -u + u^3$ and $M(u) = M_0$, where $M_0 > 0$ is constant. Let $t \in (0, T)$, $0 < T < \infty$, and $\Omega = (0, L)$. In most applications, $\Omega \in \mathbb{R}^n$ with $n = 2$ or $n = 3$ is most physically relevant. However, let us focus temporarily on the $n = 1$ case for simplicity. Thus,

$$\begin{cases} u_t = M_0\big[-u + u^3 - \epsilon^2 u_{xx}\big]_{xx}, & (x,t) \in \Omega_T, \\ u_x = M_0\big[-u + u^3 - \epsilon^2 u_{xx}\big]_x = 0, & (x,t) \in \partial\Omega_T, \\ u(x,0) = u_0(x), & x \in \Omega, \end{cases} \tag{4}$$

where $\Omega_T = (0, T) \times \Omega$ and $\partial\Omega_T = \{0, L\} \times (0, T)$. Note that $u(x, t) = \bar{u}$ constitutes a steady state of (4), where $\bar{u}$ is an arbitrary constant; however if $u(x, t)$ is to represent concentration, clearly one must assume that $0 \leqslant \bar{u} \leqslant 1$.

Let us now suppose that $u_0(x) = \bar{u} + \tilde{u}_0(x)$, where $\tilde{u}_0(x)$ represents a small perturbation from spatial uniformity. Setting $u(x, t) = \bar{u} + \tilde{u}(x, t)$, (4) yields that

$$\begin{cases} \tilde{u}_t = M_0\big[-\tilde{u} + [\bar{u} + \tilde{u}]^3 - \epsilon^2 \tilde{u}_{xx}\big]_{xx}, & (x, t) \in \Omega_T, \\ \tilde{u}_x = M_0\big[-\tilde{u} + [\bar{u} + \tilde{u}]^3 - \epsilon^2 \tilde{u}_{xx}\big]_x = 0, & (x, t) \in \partial\Omega_T, \\ \tilde{u}(x, 0) = \tilde{u}_0(x) := u_0(x) - \bar{u}, & x \in \Omega. \end{cases} \tag{5}$$

Assuming (5) to be well-posed and $\tilde{u}(x, t)$ to be small, we neglect terms which are nonlinear in $\tilde{u}(x, t)$ and obtain to leading order the linearized problem

$$\begin{cases} \tilde{u}_t = M_0\big[-\big(1 - 3\bar{u}^2\big)\tilde{u} - \epsilon^2 \tilde{u}_{xx}\big]_{xx}, & (x, t) \in \Omega_T, \\ \tilde{u}_x = M_0\big[-\big(1 - 3\bar{u}^2\big)\tilde{u} - \epsilon^2 \tilde{u}_{xx}\big]_x = 0, & (x, t) \in \partial\Omega_T, \\ \tilde{u}(x, 0) = \tilde{u}_0(x), & x \in \Omega. \end{cases} \tag{6}$$

We recall that we have assumed earlier that $0 < \epsilon^2 \ll 1$. Suppose that we optimistically neglect terms in the system (6) which contain a factor of ϵ^2. This yields

$$\begin{cases} \tilde{u}_t = -M_0(1 - 3\bar{u}^2)\tilde{u}_{xx}, & (x, t) \in \Omega_T, \\ \tilde{u}_x = -M_0(1 - 3\bar{u}^2)\tilde{u}_x = 0, & (x, t) \in \partial\Omega_T, \\ \tilde{u}(x, 0) = \tilde{u}_0(x), & x \in \Omega. \end{cases} \tag{7}$$

If we stop and consider for a moment (7), we can see that for $3\bar{u}^2 - 1 > 0$, it is equivalent to the classical diffusion equation with Neumann boundary conditions

$$\begin{cases} \tilde{u}_t = D\tilde{u}_{xx}, & (x, t) \in \Omega_T, \\ \tilde{u}_x = 0, & (x, t) \in \partial\Omega_T, \\ \tilde{u}(x, 0) = \tilde{u}_0(x), & x \in \Omega, \end{cases} \tag{8}$$

whose solutions decay to $\frac{1}{L}\int_0^L \tilde{u}_0(x)\,\mathrm{d}x$. For $3\bar{u}^2 - 1 > 0$, it is equivalent to

$$\begin{cases} \tilde{u}_t = -D\tilde{u}_{xx}, & (x, t) \in \Omega_T, \\ \tilde{u}_x = 0, & (x, t) \in \partial\Omega_T, \\ \tilde{u}(x, 0) = \tilde{u}_0(x), & x \in \Omega. \end{cases} \tag{9}$$

Now (9) is precisely the *backwards diffusion equation*, which can be obtained from the classical diffusion equation by redefining time $t \to -t$ so that time will "run backwards." The problem (9) is notoriously ill-posed as can be verified by noting that for $\tilde{u}_0 \in L^2(\Omega)$, it possesses the formal separation of variables solution

$$\tilde{u}(x, t) = \frac{A_0}{2} + \sum_{n=1}^{\infty} A_n \mathrm{e}^{\frac{n^2\pi^2}{L^2}t} \cos(n\pi x/L), \tag{10}$$

where the coefficients A_i, $i = 0, 1, 2, \ldots$, correspond to the Fourier coefficients of the initial conditions,

$$\tilde{u}(x, 0) = \tilde{u}_0(x) = \frac{A_0}{2} + \sum_{n=1}^{\infty} A_n \cos(n\pi x/L). \tag{11}$$

Its amplitude grows without bound

$$\left\|\tilde{u}(x,t)\right\|^2_{L^2[0,L]} = \frac{A_0^2}{2} + \sum_{n=1}^{\infty} A_n^2 \mathrm{e}^{\frac{2n^2\pi^2}{L^2}t}; \tag{12}$$

even for initial data based on a single mode, $\tilde{u}_0(x) = A_k \cos(k\pi x/L)$,

$$\left\|\tilde{u}(x,t)\right\|^2_{L^2[0,L]} = A_k^2 \mathrm{e}^{\frac{2k^2\pi^2}{L^2}t}. \tag{13}$$

This clearly makes little physical sense in terms of a model for phase separation, although in other contexts, such as image processing [17], it has been successfully implemented. In particular, we see that the solution, $u(x,t) = \bar{u} + \tilde{u}(x,t)$ does not remain bounded within the interval [0, 1] over time.

Thus both problems, (8) and (9), make little physical sense as models for phase separation. Hence, the higher order terms proportional to ϵ^2 are truly necessary in the physical model, and cannot be made light of easily. Seemingly this would provide a compelling reason to include such regularizing terms, but in fact regularizing terms were already added much before the dynamics for phase separation came under consideration, when equilibrium considerations lead to the search for a free energy with "phase separated" steady states possessing certain regularity and uniqueness properties. This reflects the independent scientific contribution of Gibbs (1893) [35] and van der Waals (1973) [81].

The reader should have no difficulty in ascertaining that (6), where the regularizing terms have been included, can be formulated as a well-posed problem, and it is fairly straightforward to verify that (5) and (4) can be carefully formulated as well-posed problems as well. However, before discussing existence, uniqueness, and well-posedness, we first briefly consider what are the physical phenomena one should like to model with the Cahn–Hilliard equation, and which are the most important variants of the Cahn–Hilliard equation which one should like to consider.

3. The Cahn–Hilliard equation and phase separation

We now outline what are the physical features and phenomena which one should like to be described by the Cahn–Hilliard equation. The process of phase separation in two component systems is accompanied by *pattern formation* and evolution. A typical scenario we should like to model is that of *quick quenching*. Let $\Omega \subset \mathbb{R}^3$ initially contain two components which are roughly uniformly distributed, so that $u(x,0) \approx u_0(x) \equiv \bar{u}$. We should suppose that $\bar{u} \in [0,1]$ if $u(x,t)$ is to represent concentration. If there is no flux of material into or out of Ω, then the total amount of each component should be conserved,

$$\frac{1}{|\Omega|}\int_{\Omega} u(x,t)\,\mathrm{d}x = \bar{u}, \quad 0 \leqslant t \leqslant T. \tag{14}$$

Let the initial temperature be given by Θ_0, and let the temperature of the system be now rapidly lowered (*quick quenched*) to some new temperature, $\Theta_1 \ll \Theta_0$. In two component metallic alloy systems, the average thermal conductivity is high, and the temperature of the system will equilibrate rapidly to the new temperature. With this in mind, the assumption

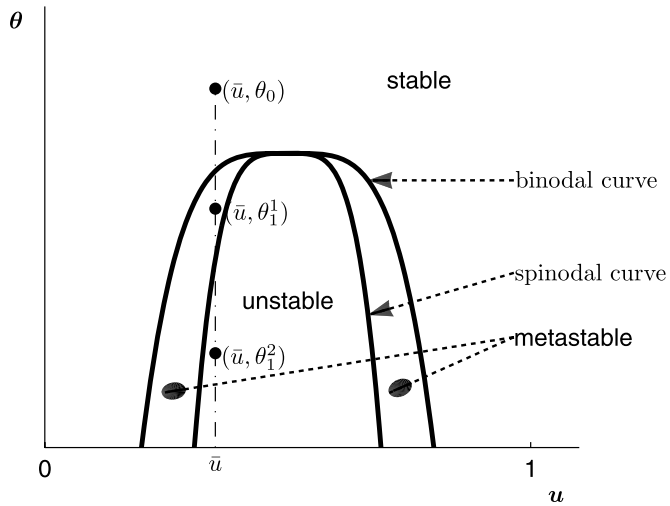

Fig. 1. A typical phase diagram. Here $(\bar{u}, \Theta_0)$ lies above the binodal curve in the stable region, $(\bar{u}, \Theta_1)$ lies in the "metastable region" which lies between the spinodal curve and the binodal curve, and $(\bar{u}, \Theta_2)$ lies below the spinodal curve.

is made that the temperature equilibrates immediately to lower temperature, Θ_1. The equilibration process can be modeled by coupling the Cahn–Hilliard equation with an energy balance equation. This augmented system is known as a *conserved phase field model* [12].

The dynamics which appears in the system Ω in the wake of quick quenching can be roughly explained with the help of *phase diagrams* as developed by Gibbs [35] within the framework of classical thermodynamics. In the present context, this implies that whether or not phase separation is predicted, as well as the nature of the phase separation which can be expected, are determined by the location of $(\bar{u}, \Theta_0)$ and $(\bar{u}, \Theta_1)$ within the phase diagram. While phase diagrams of varying levels of complexity can occur, a simplest nontrivial level of phase diagram which can describe phase separation is portrayed in Figure 1.

In the phase diagram, there are two curves which should be noted. One is an upper curve, known as the *binodal* or the *coexistence curve*, and other is a lower curve, known as the *spinodal*. The two curves intersect at point, $(\bar{u}_{\text{crit}}, \Theta_{\text{crit}})$, known as the *critical point*. If both $(\bar{u}, \Theta_0)$ and $(\bar{u}, \Theta_1)$ lie above the binodal, no phase separation is expected to occur and the system is expected to persist in its initially uniform state, $u(x, t) \equiv \bar{u}$. Hence the region above the binodal is known as the *stable* or *one-phase region*. For phase separation to occur, the initial state $(\bar{u}, \Theta_0)$ should lie above both the binodal and spinodal, and the final state $(\bar{u}, \Theta_1)$ should lie somewhere below the binodal, either above or below the spinodal.

If $(\bar{u}, \Theta_1)$ lies below the spinodal curve and $\bar{u} \neq \bar{u}_{\text{crit}}$, then phase separation is predicted to onset via *spinodal decomposition*. During the onset of spinodal decomposition, the system is distinguished by a certain "fogginess" reflecting the simultaneous growth of perturbations with many different wavelengths. Spinodal decomposition is fairly well described by the Cahn–Hilliard equation. If $(\bar{u}, \Theta_1)$ lies below the binodal but above the spinodal, phase separation can be expected to occur by *nucleation and growth*. During this process,

phase separation occurs via the appearance or *nucleation* of localized perturbations in the uniform state $\bar{u}$ which persist and grow if they are sufficiently large. Though we mention the nucleation and growth process, it is not well modeled by the Cahn–Hilliard equation, and alternative approaches have been developed for purpose such as the Lifshitz–Slyozov theory of *Oswald ripening* [49] and its extensions [42,4].

We caution the reader that if $(\bar{u}, \Theta_0)$ or $(\bar{u}, \Theta_1)$ are too close to $(\bar{u}_{\text{crit}}, \Theta_{\text{crit}})$, then the above descriptions are inappropriate, since *critical phenomena* [23], such as critical slowing down, will accompany the phase separation. Such effects are characteristic of *second order* phase transitions, as opposed to our earlier description, which was appropriate for *first order* phase transitions. Arguably Θ_1 should be taken not too far from Θ_{crit}, otherwise inertial and higher order effects may become important; these effects would render the Cahn–Hilliard model inaccurate, and make it difficult to control the phase separation process and the resultant microstructure. What distinguishes a first order phase transition from a second or higher order phase transition is the degree of continuity or regularity of the system as the system crosses from the stable regime above the binodal into the *unstable* regime which lies below it, see e.g. [50].

Whether phase separation occurs via spinodal decomposition or via nucleation and growth, eventually the system saturates into well-defined spatial domains in which one of the two components dominates, so that $u \approx u_A$ or by $u \approx u_B$, where u_A and u_B denote the binodal or limiting miscibility gap concentrations when $\Theta = \Theta_1$. See Figure 1. The average size of these spatial domains increases over time, as larger domains grow at the expense of smaller domains. This process is called *coarsening*, and the dynamics of the system may now be characterized by the motion of the boundaries or *interfaces* between these various domains. Because of mass balance, (14), the relative volume or area of the domains where $u \approx u_A$ and $u \approx u_B$ remains unchanged, but the overall amount of "domain interface" decreases as some limiting configuration is seemingly approached. While nucleation and growth is somewhat of a weak spot for the Cahn–Hilliard theory, the Cahn–Hilliard equation can give some reasonable description of the coarsening process, even if the initial stages of the phase separations were dominated by nucleation and growth.

Let us now consider two important cases of the Cahn–Hilliard equation formulation given in (1)–(3), to which we shall refer to later repeatedly.

4. Two prototype formulations

Perhaps the easiest formulation to consider is that given in (4) which was discussed in Section 2. We shall refer to this case as the *constant mobility-quartic polynomial* case, or more briefly, the *constant mobility Cahn–Hilliard equation*, and it is summarized below.

4.1. *The constant mobility – quartic polynomial case*

Let

$$M(u) = M_0 > 0, \quad \text{where } M_0 \text{ is a constant, and} \quad f(u) = -u + u^3. \tag{15}$$

It follows from (15) that

$$f(u) = F'(u), \qquad F(u) = \frac{1}{4}\big(u^2 - 1\big)^2. \tag{16}$$

Within this framework, the Cahn–Hilliard equation is given by

$$\begin{cases} u_t = M_0 \Delta(-u + u^3 - \epsilon^2 \Delta u), & (x,t) \in \Omega \times (0,T), \\ n \cdot \nabla u = n \cdot \nabla \Delta u = 0, & (x,t) \in \partial\Omega \times (0,T), \end{cases} \tag{17}$$

in conjunction with appropriate initial conditions. The value of M_0 may be set to unity by rescaling time, but we maintain M_0 in the formulation since it is frequently maintained in the literature, [62]. Note that (17) is invariant under the transformation $u \to -u$, because u in (17) represents the difference between the two concentrations, $u \equiv u_A - u_B = 2u_A - 1$. Thus, in terms of the physical interpretation, $u(x,t)$ should assume values in the interval $[-1, 1]$.

The analysis and treatment of this case is relatively easy since (17) constitutes a fourth order semilinear parabolic equation, whose treatment is similar to that of second semilinear parabolic equations such as the reaction diffusion equation,

$$u_t = \epsilon^2 \Delta u - f(u), \tag{18}$$

which arises in a wide variety of applications, from populations genetics to tiger spots, [56,57]. Nevertheless, one of the mainstays in the treatment of second order equations, the maximum principle, does not carry over easily into the fourth order setting [53]. An existence theory can be given, for example, in terms of Galerkin approximations [78] which can also be used to construct finite element approximations that can be implemented numerically. From numerical calculations and analytical consideration, it can be seen that for a sensible choice of initial conditions, (17) gives a reasonable description of spinodal decomposition and of coarsening.

An unfortunate feature of the constant mobility Cahn–Hilliard variant (17) is that its solutions need not remain bounded between -1 and 1, even if the initial data lies in this interval. This drawback can be avoided by employing a formulation, written in terms of one of the concentrations, in which the mobility is taken to degenerate when $u = 0$ and $u = 1$, and the free energy is taken to be well behaved, as was demonstrated in one space dimension by Jingxue [44]. Such a formulation does not occur so naturally in the context of phase separation, but is does occur naturally in other contexts, such as in structure formation in biofilms [46]. In the context of phase separation, it is natural in including a degenerate mobility to also include logarithmic terms in the free energy. This seemingly less natural formulation is in fact well-based in terms of the physics; the logarithmic terms reflect entropy contributions and the vanishing of the mobilities reflects jump probability considerations [72]. We shall refer to this formulation as the *degenerate mobility-logarithmic free energy case*, or for short, the *degenerate Cahn–Hilliard equation*, and it is explained below.

4.2. *The degenerate mobility – logarithmic free energy case*

Here we assume that

$$M(u) = u(1-u) \quad \text{and} \quad f(u) = F'(u), \tag{19}$$

where

$$F(u) = \frac{\Theta}{2}\big\{u \ln u + (1-u)\ln(1-u)\big\} + \alpha u(1-u), \tag{20}$$

with $\Theta > 0$, $\alpha > 0$. In (20), Θ denotes temperature, or more accurately a scaled temperature. The resultant Cahn–Hilliard formulation is now:

$$\begin{cases} u_t = \nabla \cdot M(u)\nabla\left\{\dfrac{\Theta}{2}\ln\left[\dfrac{u}{1-u}\right] + \alpha(1-2u) - \epsilon^2\Delta u\right\}, & (x,t) \in \Omega_T, \\ n \cdot \nabla u = 0, & (x,t) \in \partial\Omega_T, \\ n \cdot M(u)\left\{\dfrac{\Theta}{2u(1-u)}\nabla u - 2\alpha\nabla u - \epsilon^2\nabla\Delta u\right\} = 0, & (x,t) \in \partial\Omega_T, \end{cases} \tag{21}$$

where $\Omega_T = \Omega \times (0,T)$ and $\partial\Omega_T = \partial\Omega \times (0,T)$, and the equation and boundary conditions are to be solved in conjunction with appropriate initial data, $u_0(x)$. Since $u(x,t)$ represents here the concentration of one of the two components, $u_0(x)$ and $u(x,t)$ should satisfy $0 \leqslant u_0(x), u(x,t) \leqslant 1$.

Formally, referring to (19), (21) can be written more simply as

$$\begin{cases} u_t = \dfrac{\Theta}{2}\Delta u - \nabla \cdot M(u)\nabla\big\{2\alpha u + \epsilon^2\Delta u\big\}, & (x,t) \in \Omega_T, \\ n \cdot \nabla u = n \cdot M(u)\nabla\Delta u = 0, & (x,t) \in \partial\Omega_T. \end{cases} \tag{22}$$

Note though that (22) is in fact only meaningful for $u \in [0,1]$, and $M(u)$ has only been defined on that interval.

The mobility in (19) is referred to as a *degenerate* mobility, since it is not strictly positive. A concentration dependent mobility was already considered by Cahn in 1961 [15], and a *degenerate mobility* similar to (19) appeared in the work by Hillert in 1956 [40,39] on a one-dimensional discretely defined precursor of the Cahn–Hilliard equation. The use of logarithmic terms in the free energy, which arises naturally due to thermodynamic entropy consideration, also appeared in the papers [40,39] as well as in the 1958 paper of Cahn and Hilliard [16]. See also the discussions in [26,41]. The problem formulated in (21) constitutes a degenerate fourth order semilinear parabolic problem. Galerkin approximations can be used to prove existence and to construct finite element schemes by first regularizing the free energy. The payoff for working with the more complicated formulation is that it yields more physical results; namely, for (21) and for $\Omega \subset \mathbb{R}^n$, $n \in \mathbb{N}$, if $u_0 \in [0,1]$, then $u(x,t) \in [0,1]$ for $t \geqslant 0$. Details follow in the next section.

However, early on the degenerate and concentration dependent mobilities were replaced by constant mobilities and logarithmic terms in the free energy were expanded into polynomials, to simplify the analysis and to enable some qualitative understanding of the equation. In fact, very early analyzes were totally linear. Surprisingly this was not such a bad path to take since the dominant unstable modes are typically sustained longer that a straight forward linear analysis would suggest, see Section 6. It seems that nonlinear effects were first included by de Fontaine in 1967 [22], who did so in the context of early numerical studies of the Cahn–Hilliard equation.

For detailed derivations of both variants, see [65,66,34]. Physically speaking, it is more natural to first justify the degenerate Cahn–Hilliard equation with logarithmic free energy

terms and then to obtain the constant mobility Cahn–Hilliard equation with a polynomial free energy by making suitable approximations.

5. Existence, uniqueness, and regularity

For the constant mobility Cahn–Hilliard equation with a polynomial free energy, a proof of existence and uniqueness was given in 1986 by Elliott and Songmu [27], which also contains a finite element Galerkin approximation scheme. To be more precise, setting

$$H_E^2(\Omega) = \{v \in H^2(\Omega) \mid n \cdot \nabla v = 0 \text{ on } \partial\Omega\},$$

where n denotes the unit exterior normal to $\partial\Omega$, and $\Omega_T = \Omega \times (0, T)$, it follows from [27] that

THEOREM 5.1. *If Ω is a bounded domain in $\mathbb{R}^n$, $n \leqslant 2$, with a smooth boundary, then for any initial data $u_0 \in H_E^2(\Omega)$ and $T > 0$, there exists a unique global solution in $H^{4,1}(\Omega_T)$.*

The proof relies on Picard iteration and on a priori estimates obtained by multiplying (17) by u, $f(u)-\epsilon^2\Delta u$, and $\Delta^2 u$. By taking more regular initial data, classical solutions may also be obtained. Of some physical interest is the estimate obtained by multiplying (17) by $f(u) - \epsilon^2\Delta u$, namely

$$\mathcal{F}(t) - \mathcal{F}(0) = -\int_{\Omega_T} \left|\nabla\{f(u) - \epsilon\Delta u\}\right|^2 \mathrm{d}x\,\mathrm{d}t, \tag{23}$$

where

$$\mathcal{F}(t) = \int_\Omega \left\{F(u) + \frac{\epsilon^2}{2}|\nabla u|^2\right\} \mathrm{d}x. \tag{24}$$

The quantity $f(u) - \epsilon^2\Delta u$ is frequently identified as the chemical potential, $\mu = \mu(x, t)$.

Of interest also is the estimate obtained by multiplying (17) by $\phi \equiv 1$, namely

$$\int_\Omega u(x, t)\,\mathrm{d}x = \int_\Omega u_0(x)\,\mathrm{d}x, \tag{25}$$

which can be understood as a statement of conservation of mass or conservation of the mean.

From (23), (25), it also follows that

$$\begin{aligned}\mathcal{F}(t) - \mathcal{F}(0) &= \int_{\Omega_T} \langle f(u) - \epsilon^2\Delta u, u_t\rangle_{H^1(\Omega),(H^1(\Omega))'}\,\mathrm{d}t \\ &= -\|u_t\|^2_{L^2(0,T;H^{-1}(\Omega))},\end{aligned} \tag{26}$$

and hence the Cahn–Hilliard equation is frequently referred to as H^{-1} gradient flow.

In [58] (see [78] for an extended explanation), using essentially the same estimates and a Galerkin approximation based on the eigenfunctions of $\mathcal{A}$, where $\mathcal{A}$ is the Laplacian with Neumann boundary conditions, it is proven that

THEOREM 5.2. *For $u_0(x) \in L^2(\Omega)$, $\Omega \subset \mathbb{R}^n$, $n \leqslant 3$, there exists a unique solution, $u(x,t)$, to the constant mobility Cahn–Hilliard equation, and $u(x,t)$ satisfies*

$$u \in \mathcal{C}\big([0,T]; L^2(\Omega)\big) \cap L^2\big(0,T; H^1(\Omega)\big) \cap L^4\big(0,T; L^4(\Omega)\big), \quad \forall T > 0, \tag{27}$$

and $\mathcal{F}(t)$ decays along orbits. If, moreover, $u_0(x) \in H^2_E(\Omega)$, then

$$u \in \mathcal{C}\big([0,T]; H^2_E(\Omega)\big) \cap L^2\big(0,T; \mathcal{D}\big(\mathcal{A}^2\big)\big), \quad \forall T > 0. \tag{28}$$

To get (27), (17) needs only to be tested by u. The result (28) follows by testing (17) by $\Delta^2 u$. Uniqueness may be demonstrated by testing with the inverse of $\mathcal{A}$, suitably defined, acting on the difference of two solutions, see the discussion in [11].

Proofs of similar existence results for (17) can also be given within the framework of the theory of semilinear operators [61]. More specifically, taking $L^2(\Omega)$ to be the underlying space, and defining the $\mathcal{A}_1 = \epsilon^2\Delta$ with domain $\mathcal{D}(\mathcal{A}_1)$, the operator $\mathcal{A}_1$ can be shown to be a sectorial operator and existence may be proved by using a variation of constant formulation and results of Henry [38] and Miklavčič [54]. Within the framework of dynamical systems [61,78], it is easy to prove using (23) that

THEOREM 5.3. *As $t \to \infty$, $u(x,t)$ converges to its ω-limit cycle which is compact, connected, and invariant. If the steady states are isolated, then solutions converge to a steady state.*

In a sense, Theorem 5.3 has served as the starting point for many rich studies with regard to the identification of steady states [63,64,36,28,82–86], the existence and properties of attractors [58,59], the behavior of solutions in the neighborhood of attractors [3], the stability of steady states [61], and the list given here is admittedly very far from being complete.

As to existence theories for the degenerate Cahn–Hilliard equation, apparently the first result in this direction was given in 1992 by Jingxue [44]. The existence theory given there is for $\Omega = [0,1]$, and it is for the Cahn–Hilliard equation with a degenerate mobility but with a nonsingular free energy.

THEOREM 5.4. *Let $M(s)$ be a Hölder continuous function and $f'(s)$ be a continuous function,*

$$M(0) = M(1) = 0, \qquad M(s) \geqslant 0 \quad \textit{for } s \in (0,1).$$

Let $u_0 \in H^3_0(I)$, $0 \leqslant u_0(x) \leqslant 1$. Then problem (1)–(3) *has a generalized solution u satisfying $0 \leqslant u(t,x) \leqslant 1$.*

Here $u \in \mathcal{C}^\alpha(\bar{\Omega}_T)$, $\alpha \in (0,1)$ is said to be a *generalized solution* if
(1) $D^3 u \in L^2_{\text{loc}}(G_u)$ and $\int_{G_u} M(u)(D^3 u)^2 < \infty$, where

$$G_u = \big\{(x,t) \in \bar{\Omega}_T \mid M\big(u(x,t)\big) > 0\big\}.$$

(2) $u \in L^\infty(0,T;H^1(0,1))$, Du is locally Hölder continuous in G_u and $Du|_{\Gamma\cap G_u} = 0$ holds in the classical sense, where $\Gamma = \{\{(0,t),(1,t)\} \mid t \in [0,T]\}$.

(3) For any $\phi \in \mathcal{C}^1(\bar{\Omega}_T)$, the following integral equality holds:

$$-\int_0^1 u(x,T)\phi(x,T)\,dx + \int_0^1 u_0(x)\phi(x,0)\,dx + \int_{\Omega_T} u\phi_t + \int_{G_u} M(u)\big(\epsilon^2 D^3 u - Df(u)\big)D\phi = 0.$$

The definition of generalized solution given here and the method of proof are in the spirit of the analysis by Bernis and Friedman [9] of the thin film equation.

For the degenerate Cahn–Hilliard equation with logarithmic free energy, one has the following results due primarily to Elliott and Garcke [24,47,65],

THEOREM 5.5. *Let $\Omega \subset \mathbb{R}^n$, $n \in \mathbb{N}$, where $\partial\Omega \in \mathcal{C}^{1,1}$ or Ω is convex. Suppose that $u_0 \in H^1(\Omega)$ and $0 \leqslant u_0 \leqslant 1$. Then there exists a pair of functions $(u, \mathbf{J})$ such that*

$$\begin{aligned}
&\text{(a)} \quad u \in L^2\big(0,T;H^2(\Omega)\big) \cap L^\infty\big(0,T;H^1(\Omega)\big) \cap \mathcal{C}\big([0,T];L^2(\Omega)\big),\\
&\text{(b)} \quad u_t \in L^2\big(0,T;\big(H^1(\Omega)\big)'\big),\\
&\text{(c)} \quad u(0) = u_0 \text{ and } \nabla u \cdot n = 0 \text{ on } \partial\Omega \times (0,T),\\
&\text{(d)} \quad 0 \leqslant u \leqslant 1 \text{ a.e. in } \Omega_T := \Omega \times (0,T),\\
&\text{(e)} \quad \mathbf{J} \in L^2\big(\Omega_T, \mathbb{R}^n\big)
\end{aligned} \tag{29}$$

which satisfies $u_t = -\nabla \cdot \mathbf{J}$ in $L^2(0,T;(H^1(\Omega))')$, i.e.,

$$\int_0^T \big\langle \zeta(t), u_t(t)\big\rangle_{H^1,(H^1)'} = \int_{\Omega_T} \mathbf{J}\cdot\nabla\zeta$$

for all $\zeta \in L^2(0,T;H^1(\Omega))$ and

$$\mathbf{J} = -M(u)\nabla\cdot\big(-\epsilon^2\Delta u + f(u)\big)$$

in the following weak sense:

$$\int_{\Omega_T} \mathbf{J}\cdot\eta = -\int_{\Omega_T}\big[\epsilon^2\Delta u\nabla\cdot\big(M(u)\eta\big) + (Mf')(u)\nabla u\cdot\eta\big]$$

for all $\eta \in L^2(0,T;H^1(\Omega,\mathbb{R}^n)) \cap L^\infty(\Omega_T,\mathbb{R}^n)$ which fulfill $\eta\cdot n = 0$ on $\partial\Omega\times(0,T)$.

(f) *Moreover, letting $\mathcal{F}(t)$ be as defined in* (24), *then for a.e. $t_1 < t_2$, $t_1, t_2 \in [0,T]$,*

$$\mathcal{F}(t_2) - \mathcal{F}(t_1) \geqslant -\int_{t_1}^{t_2}\int_\Omega \frac{1}{M(u)}|\mathbf{J}|^2\,dx.$$

The proof here is based on existence results for a regularized equation, where the mobility is given by $M_\epsilon(u)$ and the free energy is given by $f_\epsilon(u)$, and implementation of an additional estimate obtained by testing the equation with ${\Phi_\epsilon}'(u)$, where ${\Phi_\epsilon}''(u) = \frac{1}{M_\epsilon}$, which yields an entropy like estimate [9], which enables the bounds $0 \leqslant u(x,t) \leqslant 1$ to be

demonstrated. We note that the "entropy" Φ, such that $\Phi''(u) = \frac{1}{M}$, had been employed earlier in the Cahn–Hilliard context in stability studies [60]. For a discussion of uniqueness and numerical schemes, see [8].

6. Linear stability and spinodal decomposition

In Section 2, linear stability of the spatially uniform state $u(x,t) = \bar{u}$ was considered in one spatial dimension for the constant mobility Cahn–Hilliard equation. Setting $\Omega = [0, L]$ and $u(x,t) = \bar{u} + \tilde{u}(x,t)$, the following linear stability problem was obtained

$$\begin{cases} \tilde{u}_t = M_0\big[-\big(1 - 3\bar{u}^2\big)\tilde{u} - \epsilon^2\tilde{u}_{xx}\big]_{xx}, & (x,t) \in \Omega_T, \\ \tilde{u}_x = M_0\big[-\big(1 - 3\bar{u}^2\big)\tilde{u} - \epsilon^2\tilde{u}_{xx}\big]_x = 0, & (x,t) \in \partial\Omega_T, \\ \tilde{u}(x,0) = \tilde{u}_0(x), & x \in \Omega. \end{cases} \tag{30}$$

It was shown in Section 2 that when ϵ is set to zero and the regularizing terms are dropped from the analysis, then (30) is equivalent to the backwards diffusion equation for $\bar{u}^2 < 1/3$, and it is equivalent to the (forward) diffusion equation for $\bar{u}^2 > 1/3$. We have already seen that when the regularizing terms in ϵ are included, then (17) is well-posed, so no problems with ill-posedness are expected here.

It is easy to verify that in the multi-dimensional case, linearization of the constant mobility Cahn–Hilliard equation about the spatially homogeneous steady state, $u(x,t) = \bar{u}$, yields the *linear stability problem*,

$$\begin{cases} \tilde{u}_t = M_0\big(\big(1 - 3\bar{u}^2\big)\Delta\tilde{u} - \epsilon\Delta^2\tilde{u}\big), & (x,t) \in \Omega_T, \\ \mathbf{n}\cdot\nabla\tilde{u} = \mathbf{n}\cdot\nabla\Delta\tilde{u} = 0, & (x,t) \in \partial\Omega_T, \\ \tilde{u}_0(x,0) = \tilde{u}_0(x), & x \in \Omega. \end{cases} \tag{31}$$

If we wish, we may proceed as in the analysis in [58,78,24] and construct a solution of (31) based on the eigenfunctions of $\mathcal{A}$, the Laplacian with Neumann boundary conditions. This yields

$$\tilde{u}(x,t) = \frac{A_0(0)}{2} + \sum_{k=1}^{\infty} A_k(0)\mathrm{e}^{\sigma(\lambda_k)t}\Phi_k(x),$$

where λ_k and Φ_k are the eigenvalues and the eigenfunctions of $\mathcal{A}$, $A_k(0)$ are the coefficients in the eigenfunction expansion for $\tilde{u}_0(x)$, and

$$\sigma(\lambda_k) = \big(\big(1 - 3\bar{u}^2\big) - \epsilon^2\lambda_k\big)\lambda_k. \tag{32}$$

One question of physical interest is number of unstable (or "growing") modes, in other words, the number of $k \in \mathcal{Z}^+$ such that $\sigma(\lambda_k) > 0$. Another question of physical interest is the identification of the dominant (or "fastest growing") mode, in other words, identifying λ_k such that $\sigma(\lambda_k)$ is maximal.

In one dimension with $\Omega = [0, L]$, $\lambda_k = (k\pi/L)^2$ and (32) yields the "dispersion relation"

$$\bar{\sigma}(k) := \sigma(\lambda_k) = \frac{k^2\pi^2}{L^2}\left[\frac{1}{4} - \frac{\epsilon^2 k^2\pi^2}{L^2}\right], \tag{33}$$

for $k \in \mathcal{Z}^+$. Examining $\bar{\sigma}(k)$ it is easily seen that $\bar{\sigma}(k)$ vanishes at $k_1 = 0$ and $k_2 = L/(2\epsilon\pi)$, it is positive for $k \in (k_1, k_2)$, it has a unique critical point (a maximum) at $k_3 = L/(2\sqrt{2}\,\epsilon\pi)$, and it is negative elsewhere. Even if $k_3 \notin \mathcal{Z}^+$, the mode k_3 is known as the *fastest growing mode*. From (33), it follows that

$$\#\text{ growing modes} = \begin{cases} \left[\dfrac{L\sqrt{1-3\bar{u}^2}}{\epsilon\pi}\right], & |\bar{u}| < \dfrac{1}{\sqrt{3}}, \\ 0, & \text{otherwise}, \end{cases} \tag{34}$$

where $[s]$ refers to the *integer value* of s. From (34), it follows that as L increases or as ϵ decreases, the number of growing modes increases. Note that if L is sufficiently small or ϵ is sufficiently large, then there are no growing modes at all. Thus the parameter range for *linear instability* depends on L and ϵ, as well as on $\bar{u}$. While ϵ reflects a material property of the system, L, which reflects the size of the system, can be varied with relative ease. Since in most systems, the size of the system is very large relative to the size of the (micro-)structures under consideration, the limit of the parameter range of instability as $\epsilon/L \to 0$ is of physical relevance. And in this limit, the parameter range for instability is given by

$$\frac{-1}{\sqrt{3}} \leqslant \bar{u} \leqslant \frac{1}{\sqrt{3}}. \tag{35}$$

The limiting compositions $\lim_{\epsilon/L\to 0} \bar{u}_\pm = \pm\frac{1}{\sqrt{3}}$ are known as the *spinodal* compositions.

What does this have to do with the way the terminology *spinodal* was used in Section 3? We note first that the one dimensional analysis may be readily generalized to higher dimensions by recalling that also in higher dimensions one has that $\lambda_k \sim k^2$. Moreover, the analysis may also be readily generalized to treat the degenerate Cahn–Hilliard equation, (21), if $\bar{u}$ is taken to lie strictly in the interval (0, 1) and perturbations are taken sufficiently small. (For the special cases, $\bar{u} = 0$ or 1, there are no perturbations which conserve the original mass constraint, and it make some physical sense to impose such a constraint.) For (21), the spinodal compositions can be easily verified to depend also on temperature, and hence the parameter range for linear stability can be prescribed in terms of $(\bar{u}, \Theta)$, as was done in Section 3.

As time goes on, the importance of the nonlinear terms becomes more and more pronounced. It is the nonlinear effects which keep the amplitude of the solution from becoming unbounded and which cause the system to saturate near the binodal values, u_A and u_B. After the initial stages of saturation, certain regions, in which u_A or u_B dominate, grow at the expense of other regions and *coarsening* begins. As the nonlinear effects set in, the differences between the two Cahn–Hilliard variants become more pronounced, as we shall see shortly. One would expect, however, that the patterning in the phase separation would be dominated by the fastest growing mode over a period of time roughly proportional to the inverse of the growth rate of the fastest growing mode. Actually, often it remains dominant over a considerably longer time interval. This rather surprising result has been demonstrated for the constant mobility Cahn–Hilliard equation, see [75,51,52].

7. Comparison with experiment

What can be said with regard to is experimental verification of the Cahn–Hilliard theory? While qualitative comparison between numerical calculation and experimental data has been known for years to be reasonable [15,43], more quantitative indicators are clearly desirable. At the onset on spinodal decomposition, linear theory predicts a *dominant growing mode* (see Section 6), and as the system evolves into phase separated domains which coarsen, the dominant length scale in the system gets larger. Two approaches have been developed to quantitatively compare the evolution of length scales.

One approach is based on the *structure function*

$$S(k,t) \equiv \left|\{u-\bar{u}\}\widehat{\ }(k,t)\right|^2,$$

where $\bar{u} = \bar{u}(t) := \frac{1}{|\Omega|}\int_\Omega u(x,t)\,\mathrm{d}x$, and "$\widehat{\ }$" denotes the Fourier transform. If the length scale characterizing the patterns of the phase separation are much smaller than the length scales of Ω, edge effects should become negligible. In this case if $\Omega \subset \mathbb{R}^2$, then

$$S(k,t) \approx \frac{1}{4\pi^2}\left|\int_{\mathbb{R}^2\times\mathbb{R}^2} f(\bar{x},t)\,f(\bar{y},t)\,\mathrm{e}^{-k\cdot(\bar{x}-\bar{y})}\,\mathrm{d}\bar{x}\,\mathrm{d}\bar{y}\right|^2, \quad \forall k \in \mathbb{R}^2, \tag{36}$$

where $f(s,t) = u(s,t) - \bar{u}(t)$. Structure function analysis can be implemented from the earliest stages of phase separation and throughout the coarsening regime. Various conjectures and predictions have been made with regard to possible self-similar behavior and scaling laws for growth of the characteristic length, based in part on analysis of the evolution of the structure factor, see e.g. [30]. Although there has been no rigorously verification of these prediction, some rigorous upper bounds on coarsening rates can be given [47,67].

Another approach which has been developed more recently is computational evaluation of Betti numbers to study the topological changes occurring during phase separation [32]. Betti numbers, β_k, $k = 0, 1, \ldots$, are topological invariants which reflect the topological properties of the structure [45]. The first Betti number, β_0 counts of the number of connected components, and the second Betti number, β_1 counts of the number of loops (in two dimensions) or the number of tunnels (in three dimensions). Reasonable qualitative agreement between theory and experiment [43] has been reported.

8. Long time behavior and limiting motions

It is constructive to be able to describe coarsening, and to obtain an accurate description of the motion of the interfaces. It turns out that to leading order, the Mullins–Sekerka problem and motion by surface diffusion give such a description. They both constitute *free boundary problems* where in the present context, the *free boundaries* refer to the interfaces between the phases. The constant mobility and the degenerate mobility Cahn–Hilliard equations differ in their behavior during coarsening stages. More specifically, the behavior of the constant mobility Cahn–Hilliard equation during coarsening can be described by the *Mullins–Sekerka* problem, and the behavior for the degenerate mobility Cahn–Hilliard equation is approximated by *surface diffusion* if $\Theta = \mathcal{O}(\epsilon^{1/2})$. It is of interest to note

that the Mullins–Sekerka problem and motion by surface diffusion appeared in various other problems, especially in materials science [55,6], long before their connection with the Cahn–Hilliard equation became known.

How does one pass from the Cahn–Hilliard equation which describes the evolution of the concentration at all points in the system, to a description of the evolution which focuses on the motion of the interfaces? One such approach is to derive limiting motions by utilizing certain formal asymptotic expansions. Such an approach was developed to describe limiting motions for the Allen–Cahn equation [74] and for the phase field equations [13], and could be generalized to the Cahn–Hilliard context by Pego [71] for the case of constant mobility and by Cahn, Elliott and Novick-Cohen [14] in the case of degenerate mobility. As to the justification of the formal asymptotic analysis, under appropriate assumptions the passage from the Cahn–Hilliard equation to the Mullins–Sekerka problem can be made rigorous [1,2,18]. The passage from the degenerate Cahn–Hilliard equation to motion by surface diffusion has yet to be rigorously justified, however numerical computations indicate that the limiting motion has been correctly identified [8].

Since during coarsening the system has already saturated into domains dominated by one of the two binodal concentrations, we can envision the domain Ω during coarsening as being partitioned by N interfaces, Γ_i, $i = 1, \ldots, N$, and the description of the evolution of the system can be given in terms of these N partitions.

8.1. *The Mullins–Sekerka problem*

In the Mullins–Sekerka problem [55], the following laws govern the evolution of the interfaces for $t \in (0, T)$, $0 < T < \infty$. See Figure 2. Away from the interfaces

$$\Delta\mu = 0, \quad x \in \Omega \backslash \Gamma, \tag{37}$$

and along the interfaces

$$V = -[n \cdot \nabla\mu]_-^+, \quad x \in \Gamma, \tag{38}$$

and

$$\mu = -\kappa. \tag{39}$$

Along $\partial\Omega$, the boundary of Ω,

$$\mathbf{n} \cdot \nabla\mu = 0, \quad x \in \Gamma \cap \partial\Omega, \tag{40}$$

and

$$\Gamma \perp \partial\Omega, \quad x \in \Gamma \cap \partial\Omega. \tag{41}$$

In (37)–(39), $\mu = \mu(x, t)$ denotes the chemical potential which in the context of the formulation of the Cahn–Hilliard equation can be identified as $\mu = f(u) - \epsilon^2 \Delta u$. Note that here, in the limiting problem, the concentration $u = u(x, t)$ no longer appears explicitly, but only via the chemical potential, μ. In (38), $V = V(x, t)$ denotes the normal velocity at the point $x \in \Gamma$, and $n = n(x, t)$ denotes an unit exterior normal to one of the components

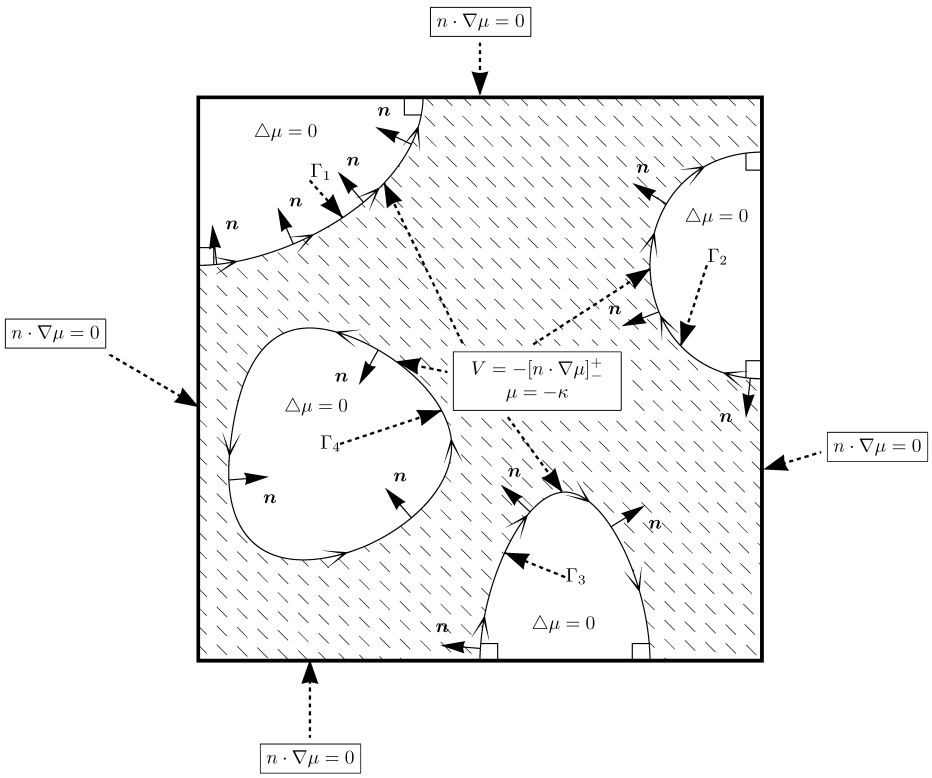

Fig. 2. Limiting motion as $t \to \infty$ for Case I: the Mullins–Sekerka problem.

Γ_i which comprises Γ. The orientations can be chosen arbitrarily for the parameterizations of the curves Γ_i, $i = 1, \ldots, N$. The normal velocity V can be defined by $V = n \cdot \vec{V}$ where $\vec{V} = \vec{V}(x, t)$ is the velocity of the interface at $x \in \Gamma$. See e.g. Gurtin [37] for background. One should note that Γ is time dependent in this formulation. In (38), $[n \cdot \nabla\mu]^+_-$ denotes the jump in the normal derivative of μ across the interface at $x \in \Gamma$. In (39), κ denotes the mean curvature. For curves in the plane,

$$\kappa = \frac{1}{R},$$

where R is the *signed radius* of the inscribed circle which is tangent to Γ at $x \in \Gamma$, and the sign of the radius is taken here to be positive if the inscribed circle lies on the "exterior" or "left" side of the curve whose orientation has been fixed. In $\mathbb{R}^3$,

$$\kappa = \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right),$$

where R_1, R_2 are the *principle radii of curvature*. See Gurtin [37] or Finn [29].

Clearly the Mullins–Sekerka problem is a *nonlocal problem* in that the motion of the interfaces cannot be ascertained without taking into account what is happening within the

domains bounded by the interfaces. For existence results for the Mullins–Sekerka problem, and a discussion of some of its qualitative properties, see for example, [2,18].

8.2. *Surface diffusion*

For the degenerate Cahn–Hilliard equation, if the scaled temperature Θ is sufficiently small and if logarithmic terms are included in the free energy, then the long time coarsening behavior can be formally shown to be governed by *surface diffusion*. By this we mean that the evolution of the interfaces $\Gamma = \Gamma_1 \cup \Gamma_2 \cup \cdots \cup \Gamma_N$ is given by

$$V = -\frac{\pi^2}{16}\Delta_s \kappa, \quad x \in \Gamma, \tag{42}$$

$$\mathbf{n} \cdot \nabla_s \kappa = 0, \quad x \in \Gamma \cap \partial\Omega, \tag{43}$$

$$\Gamma_i \perp \partial\Omega, \quad i = 1, \ldots, N,\ x \in \Gamma \cap \partial\Omega. \tag{44}$$

The boundary condition (43) is an analogue of the no-flux boundary condition, and the boundary condition (44) is a geometric analogue of the Neumann boundary condition.

In (42)–(44), V, κ and Γ have the same connotation as in our earlier discussion of the Mullins–Sekerka problem, and Δ_s denotes the *surface Laplacian* or *Laplace–Beltrami operator*, see [31]. Here the motion is *geometric* in that the motion of the interfaces is determined by the local geometry of the interfaces themselves. A formal asymptotic derivation of (42)–(44) is given in [14]. The system (42)–(44) can also be shown to describe the long time coarsening behavior for the *deep quench limit* [68].

To gain some intuition into the predicted motion, note that in the plane (see Figure 3) the system (42)–(44) can be written as

$$\begin{cases} V = -\dfrac{\pi^2}{16}\kappa_{ss}, & x \in \Gamma, \\ \kappa_s = 0, & x \in \Gamma \cap \partial\Omega, \\ \Gamma_i \perp \partial\Omega, & i = 1, \ldots, N,\ x \in \Gamma \cap \partial\Omega. \end{cases} \tag{45}$$

Here s is an arc-length parameterization of the components; i.e., along Γ_i, $i \in \{1, \ldots, N\}$,

$$s(p) = \int_{p_0}^{p} \sqrt{\dot{x}^2 + \dot{y}^2}\, \mathrm{d}\tau,$$

where $\{(x(\tau), y(\tau)) \mid p_0 \leqslant \tau \leqslant p\}$ is an arbitrary parameterization of Γ_i and p_0 refers to an arbitrary point on Γ_i. For (45), local existence can be demonstrated for smooth initial data, and perturbation of circles can be shown to evolve towards circles while preserving area [25].

9. Upper bounds for coarsening

In this section we present some rigorous results on upper bounds for coarsening. The first results given in this direction are by Kohn and Otto [47] in the context of the Cahn–Hilliard

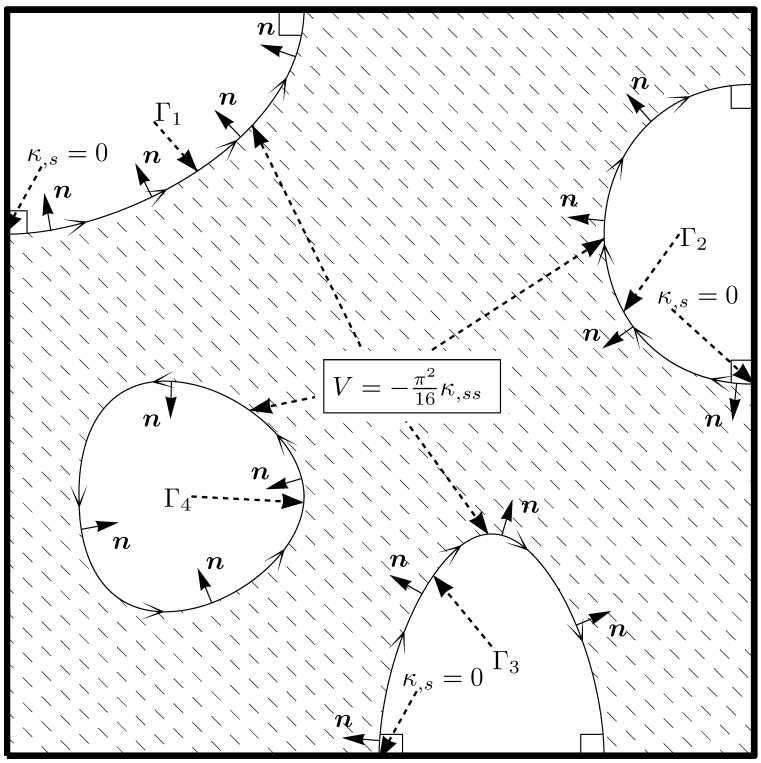

Fig. 3. Limiting motion as $t \to \infty$ for Case II: motion by surface diffusion.

equation. Their results are for (a) the Cahn–Hilliard equation with constant mobility, (17), and for (b) the degenerate Cahn–Hilliard equation, (21), where the mobility is taken as (19) and the temperature, Θ, is set to zero. The $\Theta = 0$ limit problem described in (b) in fact constitutes a free boundary obstacle problem [10], though solutions for it may be obtained via limits of solutions of (21) with $\Theta > 0$, for which the existence and regularity results of Section 5 apply. For simplicity, in [47] periodic boundary conditions are assumed and the mean mass, $\bar{u}$, is taken to be equal to $1/2$. They demonstrate upper bounds for the dominant length scale during coarsening, of the form $\propto t^{1/3}$ for (a), and of the form $\propto t^{1/4}$ for (b). Stated more precisely, they proved that there exist constants C_α such that if $L^{3+\alpha}(0) \gg 1 \gg E(0)$ and $T \gg L^{3+\alpha}(0)$, where E denotes a scaled free energy and L is a $(W^{1,\infty})^*$ norm of u, then

$$\frac{1}{T}\int_0^T E^{\theta r} L^{-(1-\theta)r}\,\mathrm{d}t \geqslant C_\alpha T^{-r/(3+\alpha)},$$

for all r, θ such that

$$0 \leqslant \theta \leqslant 1, \quad r < 3+\alpha, \quad \theta r > 1+\alpha, \quad (1-\theta)r < 2,$$

where $\alpha = 0$ for (a) and $\alpha = 1$ for (b). Their analysis is based on three lemmas which should hold at long times when the system has sufficiently coarsened. The first of these lemmas gives a bound of the form $1 \leqslant dEL$ where d is an O(1) constant, the second lemma gives a differential inequality involving E, L, and their time derivatives, and the third lemma uses the results of the first two lemmas to obtain upper bounds. Similar analyses have appeared more recently in various related settings [48,21,70].

While the predictions of Kohn and Otto are quite elegant, various deviations from the results in [47] have been seen [33,76,7], in particular strong mean mass dependence and slower than predicted rates. Moreover, the validity of their results requires that sufficiently large systems must be considered at sufficiently large times, which hinders ready numerical verification. As a partial remedy, the results of Kohn and Otto have been generalized in [67], and upper bounds for coarsening have now been given for all temperatures $\Theta \in (0, \Theta_{\text{crit}})$, where Θ_{crit} denotes the "critical temperature", and for arbitrary mean masses, $\bar{u} \in (u_A, u_B)$, where u_A and u_B denote the binodal concentrations. In [67], the domain $\Omega \subset \mathbb{R}^N$, $N = 1, 2, 3$, is taken to be bounded and convex, and the analysis applies either to the Neumann and no flux boundary conditions given in (22) or to periodic boundary conditions. Moreover, the upper bounds for the length scale are valid for all times $t > 0$, even before coarsening has truly commenced. By giving the upper bounds in terms of explicit temperature and mean mass dependent coefficients, it becomes clear that transitional and cross-over behavior may be occur, as has been reported in [33,73]. The remainder of this section is devoted to explaining some of the assumptions, analysis, and results of [47,67] in greater depth.

The starting point for the analysis in both [47,67] is the following scaled variant of the degenerate Cahn–Hilliard equation,

$$\begin{cases} u_t = \nabla \cdot \big(1-u^2\big)\nabla\left[\dfrac{\theta}{2}\ln\left[\dfrac{1+u}{1-u}\right] - u - \Delta u\right], & (x,t) \in \Omega_T, \\ n \cdot \nabla u = 0, & (x,t) \in \partial\Omega_T, \\ n \cdot \big(1-u^2\big)\nabla\left[\dfrac{\theta}{2}\ln\left[\dfrac{1+u}{1-u}\right] - u - \Delta u\right] = 0, & (x,t) \in \partial\Omega_T, \\ u(x,0) = u_0(x), & x \in \Omega, \end{cases} \tag{46}$$

which may be obtained by writing (21) in terms of the variables

$$u' = 2u - 1, \quad x' = \big(\alpha^{1/2}/\epsilon\big)x, \quad t' = \big(\alpha^2 M_0/\epsilon^2\big)t, \quad \theta = \Theta/\alpha, \tag{47}$$

then dropping the primes. In the context of (46), $\theta = 1$ corresponds to the critical temperature. By setting $\theta = 1 - \delta$, $x' = (\delta/2)^{1/2}$, $t' = (\delta^2/4)t$, and $u' = (3\delta)^{-1/2}u$ in (46), and letting $\delta \to 0$ and dropping the primes, the constant mobility Cahn–Hilliard equation, (17), with $M_0 = 1$ is obtained. For this reason, case (a) treated in [47] is referred to there as the "shallow quench" limit. Letting $\theta \to 0$ in (46), case (b), which is referred to in [47] as the "deep quench" limit, is obtained.

Why consider $E^{-\lambda}(t)L^{1-\lambda}(t)$, $0 \leqslant \lambda \leqslant 1$, as a reasonable measure for the dominant length scale in the system? Since the mean mass, $\bar{u} = \frac{1}{|\Omega|}\int_\Omega u(x,t)\,\mathrm{d}x$, is time invariant for (46), it is convenient to define a first length scale, $L(t)$ as

$$L(t) := \sup_{\xi \in A} \frac{1}{|\Omega|}\int_\Omega u(x,t)\,\xi(x)\,\mathrm{d}x,$$

where

$$A := \left\{ \xi \in W^{1,\infty} \;\middle|\; \int_\Omega \xi \, \mathrm{d}x = 0 \text{ and } \sup_\Omega |\nabla \xi| = 1 \right\}.$$

A second length scale, $E^{-1}(t)$, can be defined based on the free energy, $\mathcal{F}(t)$, which was introduced in (24). In terms of the rescalings (47), we obtain that

$$E(t) := \frac{1}{|\Omega|}\mathcal{F}(t) = \frac{1}{2|\Omega|}\int_\Omega \left\{ |\nabla u|^2 + \left[\frac{\partial W}{\partial u} \right]^2 \right\}_{|_{u=u(x,t)}} \mathrm{d}x, \tag{48}$$

where

$$\frac{\partial W}{\partial u} = \left[\left(1-u^2\right) + \theta\left\{ (1+u)\ln(1+u) + (1-u)\ln(1-u) \right\} + e(\theta) \right]^{1/2}. \tag{49}$$

In (49), $e(\theta)$ is determined by requiring that $\frac{\partial W}{\partial u} = 0$ at $u = u_\pm$, where $u_\pm$ denote here the two unique minima of $\frac{\partial W}{\partial u}$, such that $u_+ = -u_- > 0$. A straightforward calculation yields that

$$\theta = \frac{2u_\pm}{\ln(1+u_\pm) - \ln(1-u_\pm)} = \left[\sum_{k=0}^{\infty} \frac{1}{2k+1} u_\pm^{2k} \right]^{-1}, \tag{50}$$

and hence, in particular, $u_\pm = u_\pm(\theta)$, as one would expect. That $E^{-1}(t)$ acts as a length scale measuring the amount of perimeter during coarsening can be seen by noting that (48) implies that

$$E(t) \geqslant \frac{1}{|\Omega|}\int_\Omega \left| \nabla W(u) \right| \mathrm{d}x. \tag{51}$$

During the later stages of coarsening when the system is approximately partitioned into regions in which $u = u_+$ and in which $u = u_-$, the inequality in (51) can be expected to be closely approximated by equality. The expression on the right-hand side of (51) scales as length^{-1} and gives, for such partitioned systems, a measure of the amount of interfacial surface area per unit volume times the "surface energy", $\sigma = W(u_+) - W(u_-)$. Note that for well partitioned systems, $(u_+ - u_-)\|u\|_{W^{1,\infty}}^{-1}$ gives a rough lower bound on interfacial widths, hence $|\Omega|(u_+ - u_-)^{-1}\|u\|_{W^{1,\infty}}$ gives an upper bound on the amount of interfacial area within the volume $|\Omega|$, and therefore, in some sense, $L(t)$ and $E^{-1}(t)$ are measuring similar quantities. If $L(t)$ and E^{-1} both act as reasonable measures of "length" during coarsening, clearly $E^{-\lambda}L^{(1-\lambda)}(t)$, $0 \leqslant \lambda \leqslant 1$ also constitutes a reasonable measure.

In treating temperatures $\theta \in [0,1]$ and mean masses $u_- < \bar{u} < u_+$, the following technical results are useful:

CLAIM 9.1. *Let* $0 < \theta < 1$, $u_- < \bar{u} < u_+$, *and let* $u(x,t)$ *denote a solution to* (46). *Then*

$$\frac{\partial W}{\partial u}(u) \geqslant \Psi(\theta)\left| u^2 - u_\pm^2 \right|,$$

where

$$\Psi(\theta) := \frac{1}{u_\pm^2}\left[-1 + \frac{2}{u_\pm}\left\{ \frac{\ln(1-u_\pm) + \ln(1+u_\pm)}{\ln(1-u_\pm) - \ln(1+u_\pm)} \right\} \right],$$

and

$$\frac{1}{|\Omega|}\int_\Omega \left(u_\pm^2 - u^2\right) \mathrm{d}x \leqslant 2[E + \theta \ln 2].$$

The following lemmas [67], which make use of the estimates in Claim 9.1, are extensions and generalization Lemmas 1, 2, and 3 from [47].

LEMMA 9.1. *Let* $0 < \theta < 1$ *and* $u_- < \bar{u} < u_+$. *Then*

$$\left(u_\pm^2 - \bar{u}^2\right) \leqslant \left[32L(t)\left(\frac{5E(t)}{u_+[\Psi(\theta)]^{1/2}} + \frac{3|\partial\Omega|}{|\Omega|}\right)\right]^{1/2} + F(E;\theta), \quad 0 < t, \tag{52}$$

where

$$F(E;\theta) = \min\left\{\left[\frac{2E}{\Psi(\theta)}\right]^{1/2}, 2[\theta \ln 2 + E]\right\}. \tag{53}$$

LEMMA 9.2. *Let* $0 < \theta < 1$ *and* $u_- < \bar{u} < u_+$. *Then*

$$|\dot{L}|^2 \leqslant -\left(1 - u_\pm^2\right)\dot{E} - F(E;\theta)\dot{E}, \quad 0 < t, \tag{54}$$

where $F(E;\theta)$ *is as defined in* (53).

LEMMA 9.3. *Suppose that*

$$|\dot{L}|^2 \leqslant -AE^\alpha \dot{E}, \quad 0 \leqslant t \leqslant T, \tag{55}$$

where

$$0 \leqslant \alpha \leqslant 1, \quad 0 \leqslant \varphi \leqslant 1, \quad r < 3 + \alpha, \quad \varphi r > 1 + \alpha, \quad (1 - \varphi)r < 2. \tag{56}$$

If, in addition to (55), (56),

$$LE \geqslant B, \quad 0 \leqslant t \leqslant T, \tag{57}$$

then

$$\frac{1}{T}\left[\int_0^T E^{r\varphi} L^{-(1-\varphi)r}\, \mathrm{d}t + L(0)^{(3+\alpha)-r}\right] \geqslant \vartheta_1 T^{-r/(3+\alpha)}, \tag{58}$$

where $\vartheta_1 = \vartheta_1(A, B, \alpha, r, \varphi)$.

If, in addition to (55), (56),

$$E \geqslant C, \quad 0 \leqslant t \leqslant T, \tag{59}$$

then

$$\frac{1}{T}\left[\int_0^T E^{\varphi r} L^{-(1-\varphi)r}\, \mathrm{d}t + L(0)^{2-(1-\varphi)r}\right] \geqslant \vartheta_2 T^{-(1-\varphi)r/2}, \tag{60}$$

where $\vartheta_2 = \vartheta_2(A, C, \alpha, r, \varphi)$.

REMARK 9.1. The inequalities in (56) imply that $\frac{2}{1-\varphi} > 3 + \alpha$, hence the upper bound predicted by (60) is slower than in (58).

We shall now see how Lemmas 9.1, 9.2, and 9.3 imply upper bounds for coarsening. Let us first consider the expression for $F(E;\theta)$. If $0 < \theta < 1$ and E is sufficiently small, then $F(E;\theta) = [2E/\Psi(\theta)]^{1/2}$. If the term $\frac{3|\partial\Omega|}{|\Omega|}$ in (52), which represents boundary effects, is sufficiently small, Lemma 9.1 can be used to imply either a bound of the form (57) or a bound of the form (59). In particular, if E is sufficiently small, then a bound of the form (57) is implied. It now follows from Lemma 9.2, depending on the relative size of the terms $(1 - u_{\pm}^2)$ and $[2E/\Psi(\theta)]^{1/2}$, that Lemma 9.3 holds with either $\alpha = 0$ or $\alpha = 1/2$. In particular, if E is sufficiently small, then Lemma 9.3 holds with $\alpha = 0$. This yields the shallow quench result of [47].

Suppose that $\theta = 0$. If E is sufficiently small, then $F(E;\theta) = 2E$. Again, Lemma 9.1 can be seen to imply either a bound of the form (57) or a bound of the form (59), with a bound of the form (57) being implied if E is sufficiently small. When $\theta = 0$, then referring to (50), $u_{\pm} = \pm 1$. Hence if $F(E;\theta) = 2E$, Lemma 9.2 implies that (55) holds with $\alpha = 1$. This yields the deep quench result of [47].

More generally, Lemmas 9.1 and 9.2 can be used to demonstrate that if $\bar{u} \in (u_-, u_+)$ and $\theta \in [0, 1)$, then for any $t > 0$, there exists times $0 \leqslant T_1 < T_2$ such that for all $t \in (T_1, T_2)$, (55) holds for some $\alpha \in \{0, \frac{1}{2}, 1\}$ and either (57) or (59) holds. Noting the autonomy of the differential inequality, (55), it is possible to conclude

THEOREM 9.1. *Let $u(x,t)$ be a solution to* (46) *in the sense of Theorem* 5.5 *such that $u_- < \bar{u} < u_+$ and $0 < \theta < 1$, then at any given time $t \geqslant 0$, if boundary effects are negligible then upper bounds of the form*

$$\frac{1}{t - T_1}\left[\int_{T_1}^{t} E^{r\varphi} L^{-(1-\varphi)r}\,\mathrm{d}t + L(T_1)^{(3+\alpha)-r}\right] \geqslant \vartheta_1 (t - T_1)^{-r/(3+\alpha)},$$

or

$$\frac{1}{t - T_2}\left[\int_{T_2}^{t} E^{\varphi r} L^{-(1-\varphi)r}\,\mathrm{d}t + L(T_2)^{2-(1-\varphi)r}\right] \geqslant \vartheta_2 (t - T_2)^{-(1-\varphi)r/2},$$

may be prescribed, for appropriate values of the parameters.

The boundary terms, which are neglected in Theorem 9.1, may be incorporated by suitably redefining E. Over time, E decreases, and the relative size of the terms on the right-hand side of (52), (54) changes in accordance also with the size of $\bar{u}$ and θ. In this manner, a variety of time depend predictions for upper bounds on coarsening follow from Theorem 9.1, with transitions which may clearly depend on both $\bar{u}$ and θ, [67,76,33]. A complete discussion of these results is quite involved [67], and a complete understanding of the actual coarsening rates requires refinement of the bounds [20] and considerable further work.

A CLOSING REMARK. Roughly fifty years have passed since the Cahn–Hilliard equation was proposed as a model for phase separation [16,15]. While many aspects of its dynamics

have been studied, many aspects remain to be analyzed. The author of this chapter apologies that the list of references which follow cannot claim to be complete. Clearly it is a tribute to the robustness of the equation, that the details that have been forthcoming from the analysis all seem to contribute to the overall picture and not to lead to the dismissal of the model. The Cahn–Hilliard equation continues to be proposed as a relevant model in a variety of new contexts, and it continues to be generalized in a variety of new directions, [62,65].

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