

Upper Bounds for Coarsening: Temperature and Concentration Dependence

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Keywords: Cahn-Hilliard equation, coarsening, temperature dependence, degenerate mobility

Abstract

We analyze temperature and mean concentration effects on coarsening within the framework of the Cahn-Hilliard equation with degenerate mobility and based on a free energy containing logarithmic terms. We demonstrate that coarsening rates may depend on both concentration and on temperature, and that time dependent transitions in the coarsening rate can occur during the coarsening process. Our results here extend and generalize the results of Kohn & Otto [1].

1. Introduction

During the later stages of phase transitions, the overall length scale of the system grows as certain of the regions dominated by one of the energy minimizing phases grow at the expense of others. This process is known as coarsening. In many technical applications, it is important to be able to predict the coarsening rate as often the coarsening process does not come to completion on laboratory time scales and hence a partially coarsened specimen constitutes the final product. This is the situation in the production of polymeric sponges and gels, for example. Thus it is of interest to determine the coarsening rates and their time dependence, and how they depend on the control parameters of the system, such as the mean concentration and the ambient temperature.

We consider these questions within the framework of the Cahn-Hilliard equation with a concentration dependent mobility and based on a free energy which includes entropic logarithmic terms and temperature dependence,

$$u_t = \nabla \cdot M(u) \nabla [\theta \{ \ln u - \ln(1-u) \} - \alpha u - \varepsilon^2 \Delta u] \quad (1).$$

Here $u = c_A$ is the concentration of one of two components in a two component system, θ is a scaled temperature, and $M(u) \geq 0$ is the scaled mobility. Since it is reasonable to assume that $M(u) = u(1-u)$, (1) constitutes a degenerate parabolic equation. We shall refer to (1) as the *degenerate Cahn-Hilliard equation*.

1.1 The degenerate Cahn-Hilliard equation

Though the degeneracy of the mobility and the inclusion of the logarithmic terms in (1) may appear to be an unnecessarily cumbersome alternative to the more familiar constant mobility-polynomial free energy variant of the Cahn-Hilliard equation,

$$u_t = \Delta(-u + u^3 - \varepsilon^2 \Delta u) \quad (2),$$

in fact the inclusion of the logarithmic terms and the degenerate mobility is useful, as it guarantees for example that the solution u satisfies $u \in [0,1]$ at all times, if it did so initially. From the point of view of coarsening, within the framework of (1), it is possible to ascertain coarsening predictions for all temperatures between $\theta = 0$ and $\theta = \theta_{crit} (= \alpha / 2)$, and for all mean concentrations \bar{u} lying within the miscibility gap, $[u_-, u_+]$, where u_{\pm} denote the binodal concentrations which, within the context of (1), satisfy $u_- = -u_+$. The degenerate Cahn-Hilliard formulation, (1), arises quite naturally in the context of phase separation, as can be seen by referring back to the original papers of Cahn and Hilliard [2,3]. Somewhat similar formulations arise for example in the context of biofilm structure formation, [4]. Applications of the Cahn-Hilliard equation also occur in the context of phase separation (spinodal decomposition and coarsening), thin film dynamics, image processing, population dynamics, river bed formation, galaxy structure formation, and biofilm structure formation. See [5,6] for a survey and review of the Cahn-Hilliard literature, and for a detailed comparison of the Cahn-Hilliard models, (1) and (2).

The Cahn-Hilliard equation (1) may be expressed as

$$u_t = \nabla \cdot M(u) \nabla \mu, \quad \mu = f(u) - \varepsilon^2 \Delta u,$$

where μ is the chemical potential, and

$$M(u) = u(1-u), \quad f(u) = \theta \{\ln u - \ln(1-u)\} - \alpha u.$$

It is reasonable to impose Neumann boundary conditions, $n \cdot \nabla u = 0$, as well as no-flux boundary conditions, $n \cdot J = 0$ with $J = \nabla \mu$, unless experimental conditions indicate otherwise. The formulation given in (1) is more accurate than (2) in certain applications, especially if the values $u = 0$ or $u = 1$ are realized by the boundary conditions, as occurs naturally in the context of diffusion couples [7]. The assumption $M(u) = u(1-u)$ makes fairly good physical sense, since mobilities should vanish at the pure phases $u = 0$ and $u = 1$ based on jump probability considerations, [8].

1.2 Comparison of the Cahn-Hilliard models, (1) and (2).

For (1), as for (2), if initially $u_0(x) = \bar{u} + \tilde{u}_0(x)$, where \bar{u} lies within the linearly unstable spinodal region and \tilde{u}_0 is a sufficiently small perturbation, then at early times the onset of phase separation occurs via spinodal decomposition and dominance of a "fastest growing mode,"

yielding exponential growth of certain perturbations, can be seen. During the later stages of phase separation, coarsening takes place and the differences between the degenerate and the constant mobility cases become more pronounced. For the constant mobility Cahn-Hilliard equation, (2), during the later stages of phase separation, the evolution of the system is approximately governed by the dynamics of the Mullins-Sekerka problem. For (1), the Cahn-Hilliard equation with degenerate mobility, during the later stages of phase separation, the motion of the system is known to be governed by motion by surface diffusion, although this has yet to be justified rigorously. See also the discussion in [9].

1.3 Upper bounds on coarsening

During coarsening, as certain grains or regions dominated by one of the energy minimizing phases grow at the expense of others, the overall length scale of the system gradually increases. A question which has aroused considerable interest is whether or not power law bounds may be prescribed for the rate of growth. The first rigorous results in this direction were obtained by Kohn and Otto [1]. They demonstrated that if $l(t)$ represents a typical length scale for the system, then for (1), when $\theta \uparrow \alpha/2$, and for (2), there is an upper bound of the form $t^{1/3}$ for $l(t)$, after a sufficient coarsening has occurred. For (1), in the limit $\theta \downarrow 0$, a similar upper bound of the form $t^{1/4}$ was demonstrated for $l(t)$. Recently in [10], we have extended these results, finding how the transition between the predicted $t^{1/4}$ and $t^{1/3}$ bounds arises as the temperature θ and the mean concentration \bar{u} are varied. Our results also indicate that under appropriate conditions, $t^{2/7}$ upper bounds may also occur. These results are explained further in the next section.

2. Upper bounds on coarsening

To obtain a more symmetric formulation, we rescale (1), introducing the variables and parameters: $\tilde{u} = (2u - 1)$, $\tilde{x} = (\alpha^{1/2} / \varepsilon)x$, $\tilde{t} = (\alpha^2 / \varepsilon^2)t$, $\tilde{\theta} = \theta / \alpha$, then dropping the tildes for sake of notational simplicity. Note that in the context of the new scaling, $\theta_{crit} = 1$.

2.1 Two length scales

Following [1], two lengths scales are defined, $L(t)$ and $E^{-1}(t)$, where

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

where $A := \left\{ \xi \in W^{1,\infty} \mid \int_{\Omega} \xi dx = 0, \sup_{\Omega} |\nabla \xi| = 1 \right\}$, and

$$E(t) := \frac{1}{2|\Omega|} \int_{\Omega} \left\{ |\nabla u|^2 + \left[\frac{\partial W}{\partial u} \right]^2 \right\} dx,$$

where $\frac{\partial W}{\partial u} = \left[(1-u^2) + \theta \{ (1+u) \ln(1+u) + (1-u) \ln(1-u) \} + e(\theta) \right]$ and $e(\theta)$ is determined by requiring that $\frac{\partial W}{\partial u} = 0$ when $u = u_{\pm}$. The typical length scale of the system, $l(t)$, is taken as the weighted combination of $L(t)$ and $E(t)$, $L^{\phi}(t)E^{(1-\phi)}(t)$ with $0 \leq \phi \leq 1$. Ideally one should prefer to work with a simpler expression for $l(t)$, though this is often not so easy to accomplish.

2.2 Two lemmas

In the spirit of [1], we obtain that if boundary effects can be neglected, then

Lemma 1. If $0 < \theta < 1$ and $u_- < \bar{u} < u_+$, then when $t > 0$,

$$1 \leq A + \min \{ B_1, B_2 \}, \quad (3)$$

and

$$|\dot{L}(t)|^2 \leq -(1-u_{\pm}^2)\dot{E}(t) - (u_{\pm}^2 - \bar{u}^2) \min \{ B_1, B_2 \} \dot{E}(t), \quad (4)$$

where

$$A = \frac{1}{(u_{\pm}^2 - \bar{u}^2)} \left[32L(t) \left(\frac{5E(t)}{u_+ [\Psi(\theta)]^{1/2}} \right) \right]^{1/2}, \quad B_1 = \frac{1}{(u_{\pm}^2 - \bar{u}^2)} \left[\frac{2E(t)}{\Psi(\theta)} \right]^{1/2}, \quad B_2 = \frac{2}{(u_{\pm}^2 - \bar{u}^2)} [\theta \ln 2 + E(t)],$$

and

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

Lemma 2. Suppose that for $0 \leq t \leq T$, and

$$|\dot{L}(t)|^2 \leq -CE^{\gamma} \dot{E}(t), \quad 0 \leq \gamma \leq 1. \quad (5)$$

i) If, moreover,

$$L(t)E(t) \geq D_1, \quad 0 \leq t \leq T, \quad (6)$$

then

$$\frac{1}{T} \left[\int_0^T E^{r\phi} L^{-(1-\phi)r} dt + L(0)^{(3+\gamma)-r} \right] \geq \mathcal{G}_1 T^{-r/(3+\gamma)}, \quad (7)$$

where $0 \leq \phi \leq 1, r < 3 + \gamma, \phi r > 1 + \gamma, (1 - \phi)r < 2$, and $\mathcal{G}_1 = \mathcal{G}_1(C, D_1, \gamma, r, \phi)$.

ii) If, moreover,

$$E(t) \geq D_2, \quad 0 \leq t \leq T, \quad (8)$$

then

$$\frac{1}{T} \left[\int_0^T E^{r\phi} L^{-(1-\phi)r} dt + L(0)^{2-(1-\phi)r} \right] \geq \mathcal{G}_2 T^{-(1-\phi)r/2}, \quad (9)$$

where $0 \leq \phi \leq 1, r < 3 + \gamma, \phi r > 1 + \gamma, (1 - \phi)r < 2$, and $\mathcal{G}_2 = \mathcal{G}_2(C, D_2, \gamma, r, \phi)$.

The proofs of Lemma 1 and Lemma 2 are given in [10]. The implications of these lemmas in terms of coarsening bounds is explained in the subsection which follows.

2.3 The implied upper bounds on coarsening

Let us first consider Lemma 1. Note that $\min\{B_1, B_2\} = B_1$, when $0 < E(t) < E_-$ or $E_+ < E(t)$, and $\min\{B_1, B_2\} = B_2$ when $E_- < E(t) < E_+$, where $E_{\pm} = \frac{1}{4\psi} \left[1 - (4 \ln 2)\theta\psi \pm \sqrt{1 - (8 \ln 2)\theta\psi} \right]$.

As it can be demonstrated that for all $0 \leq t$, $\dot{E}(t) \leq 0$, if initially $E(0)$ is sufficiently large, then transitions can be seen in the relative size of B_1 and B_2 as $E(t)$ becomes smaller.

The predicted upper bounds can now be ascertained, based on the size of $E(t)$.

i) Suppose that $\min\{B_1, B_2\} = B_1$. By considering (3), it can be seen that a bound of the form (6) is predicted if $0 < E < E_{11}$, where $E_{11} = u_{\pm}^4 \psi (1 - (\bar{u}^2 / u_{\pm}^2)) / 8$, and a bound of the form (8) is predicted if $E > E_{11}$. From (4), it can be seen that (5) holds with $\gamma = 0$ if $0 < E < E_{12}$, where $E_{12} = \psi (1 - u_{\pm}^2)^2 / 2$, and (5) holds with $\gamma = 1/2$ if $E > E_{12}$.

ii) Suppose that $\min\{B_1, B_2\} = B_2$. By again considering (3), it can be seen that a bound of the form (6) is predicted if $0 < E < E_{21}$, where $E_{21} = u_{\pm}^2(1 - (\bar{u}^2 / u_{\pm}^2)) / 4 - \theta \ln 2$, and a bound of the form (8) is predicted if $E > E_{21}$. From (4), it can be seen that (5) holds with $\gamma = 0$ if $0 < E < E_{22}$, where $E_{22} = (1 - u_{\pm}^2) / 2 + \theta \ln 2$, and (5) holds with $\gamma = 1$ if $E > E_{22}$.

Note that energy levels $E_{\pm}, E_{11}, E_{12}, E_{21}, E_{22}$ depend on the mean concentration, \bar{u} , and on the temperature, θ . Moreover, it can be readily seen that in fact the relative size of these values changes as \bar{u} and θ are varied. From these considerations and by noting that the differential inequality (5) is autonomous, the transitions and rates indicated earlier can be ascertained. For further details and analysis, see [10] and [11].

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