The Cahn-Hilliard Equation and Upper Bounds on Coarsening

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The Cahn-Hilliard equation

Cahn and Hilliard introduced the equation:

(1)
$$\begin{cases} u_t = \nabla \cdot M(u)\nabla\{f(u) - \epsilon^2 \triangle u\}, & (x,t) \in \Omega_T, \\ n \cdot \nabla u = n \cdot \nabla\{f(u) - \epsilon^2 \triangle u\} = 0, & (x,t) \in \partial\Omega_T, \\ u(x,0) = u_0(x), & x \in \Omega, \end{cases}$$

in 1958, 1961 to model phase separation in binary alloys. In (1), $u(x,t)$ is the *concentration* of one of the two components of a binary alloy, $M(u) \geq 0$ is the *mobility coefficient,* and $f(u) = F'(u)$, where $F(u)$ is the *homogeneous* contribution to the free energy.

We shall assume that $\Omega \subset \mathbb{R}^N$, $N = 1, 2, 3$ is *bounded* and *convex*.

Since $u(x,t)$ is a *concentration*, it should satisfy $0 \leq u_0(x),\ u(x,\ t) \leq 1.$

Often (1) is not completely accurate, as it neglects *anisotropy*, *elastic effects*, *thermal effects*, *coupling to fluid flow*. Nevertheless, the simple model (1) is important, as it also models *population dynamics*, *galaxy formation*, *biofilm structure formation*, *swarm formation*, and more.

Cahn-Hilliard dynamics

In order to understand phase separation, let's consider the evolution of a system which is *initially nearly spatially uniform* at a *linearly unstable concentration.*

If such a system is *rapidly cooled* or *quenched* into a region in the thermodynamic phase diagram where the mean concentration is *linearly unstable,* then phase separation onsets.

During the initial stages of phase separation, a *dominance of the* length scale predicted by the *fastest growing* or "most unstable" mode will be apparent, until the system *locally saturates* near equilibrium phases.

Afterwards, *certain* of the saturated *regions grow as others shrink,* and the overall length scale of the system increases. This is the process known as *coarsening*.

To understand the coarsening process, it is instructive to define some *dominant length scale*, $l(t)$, and to analyze its development. Often $l(t)$ has been said to exhibit *scaling behavior*.

Some numerics...

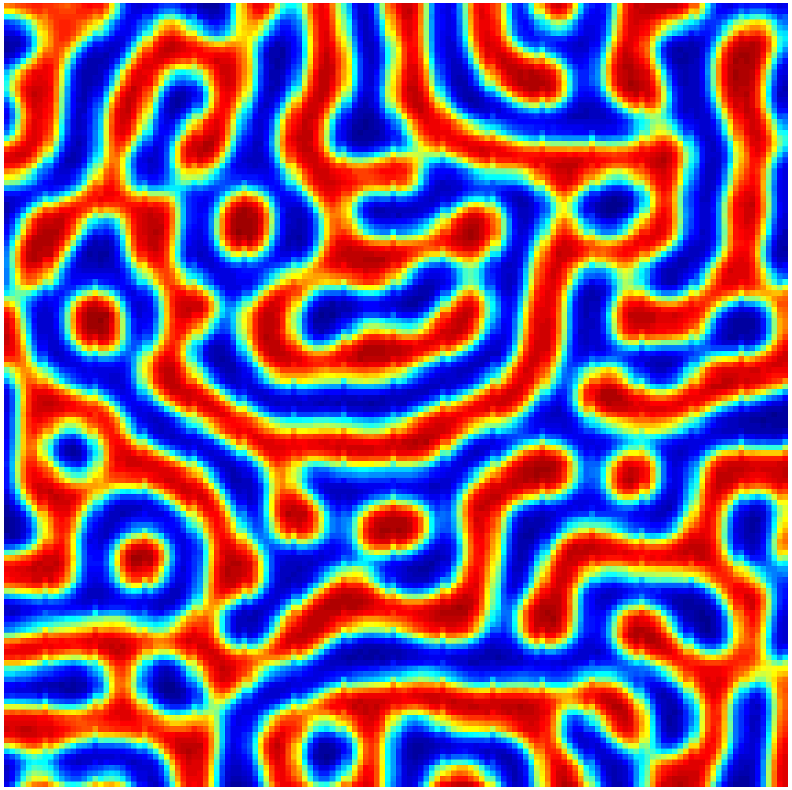


Figure 1: Early stages of evolution (D. Eyre).

Some numerics...

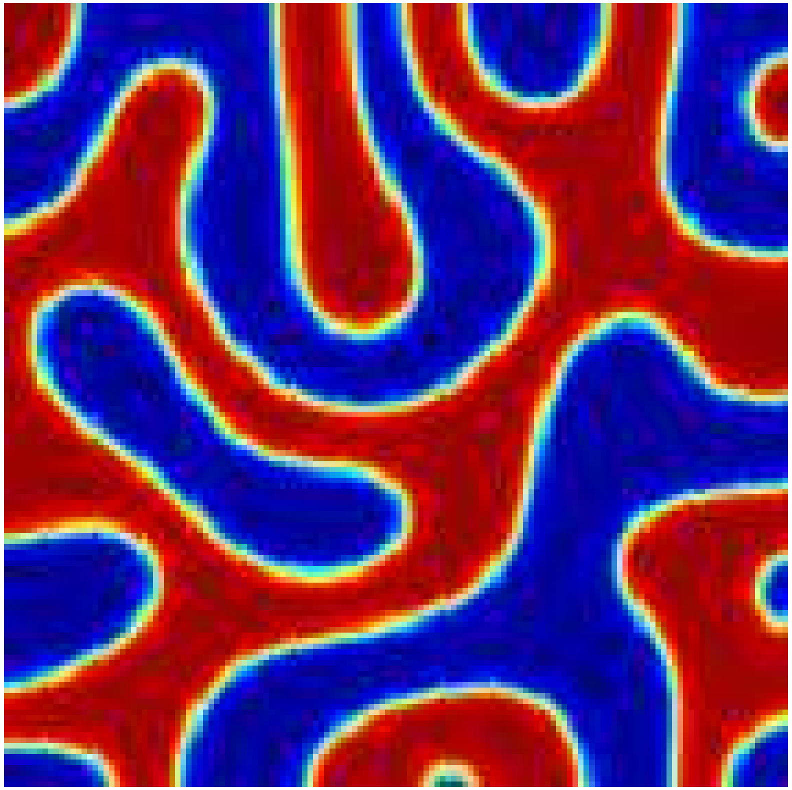


Figure 2: Middle stages of evolution

Some numerics...

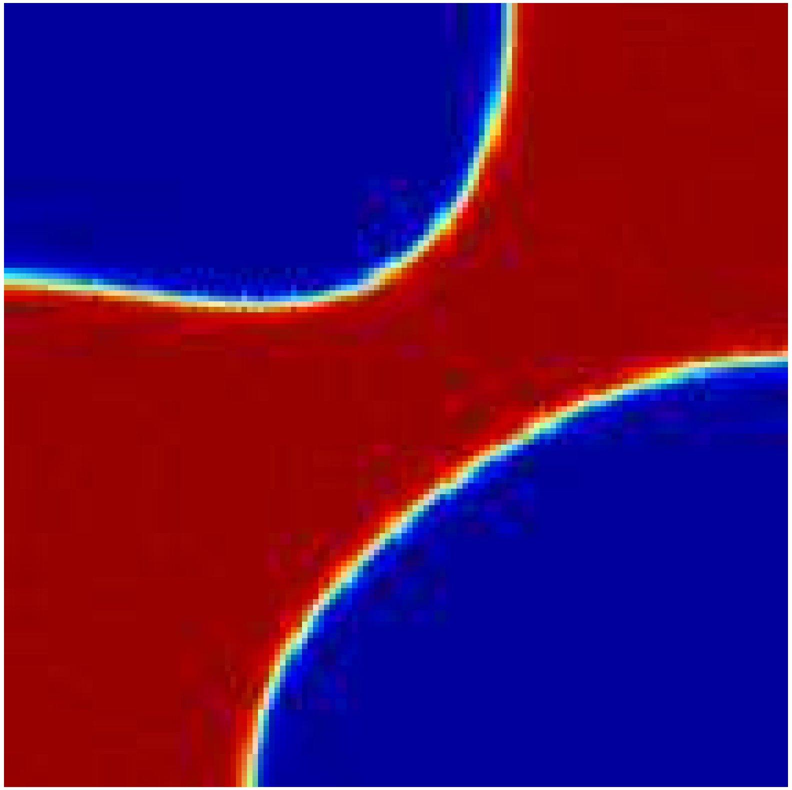


Figure 3: Late stages of evolution

The derivation

The variables u_1, u_2, describe the two components, via their volume or molar fractions. Conservation of mass implies that in the absence of reactions producing or destroying either of the two components,

(2) $$u_{1t} = -\nabla \cdot \mathbf{J_1}, \quad u_{2t} = -\nabla \cdot \mathbf{J_2},$$

where $\mathbf{J_i}$ is the flux of u_i, $i = 1,\ 2$.

Relying on non-equilibrium thermodynamics (Gibbs, Onsager), we take there to be two *chemical potentials*, μ_1, μ_2, corresponding to the two components in the system. This implies there to be two *driving forces* in the system, $\nabla\mu_1$, $\nabla\mu_2$. Non-equilibrium thermodynamics now implies that

(3) $$\mathbf{J_1} = -L_{11}\nabla\mu_1 - L_{12}\nabla\mu_2, \quad \mathbf{J_2} = -L_{21}\nabla\mu_1 - L_{22}\nabla\mu_2,$$

where L_{ij}, are *phenomenological coefficients*.

Microscopic reversibility (the requirement that at a microscopic level all motions are reversible) implies that L is *symmetric*, and the *second law of thermodynamics* (non-negativity of the entropy production) implies that L is *non-negative definite*.

Mass conservation requires that

(4) $$\mathbf{J_1} + \mathbf{J_2} = 0.$$

To guarantee (4), we set $L_{12} + L_{22} = L_{11} + L_{21} = 0$. Now, since L is symmetric and non-negative definite,

(5) $$L_{11} = L_{22} = -L_{12} = -L_{21} \geq 0.$$

If either $u_1(x,\, t) \equiv 0$ or 1, there is no local mass flux. Thus we may set

(6) $$L_{ij} = u_1 u_2 \widetilde{L}_{ij}, \quad l = \widetilde{L}_{11} \geq 0,$$

yielding

(7) $$\mathbf{J_1} = -l\, u_1 u_2 \nabla(\mu_1 - \mu_2), \quad \mathbf{J_2} = -l\, u_1 u_2 \nabla(\mu_2 - \mu_1),$$

and thus that

(8) $$\frac{\partial u_1}{\partial t} = \nabla \cdot (l u_1 u_2) \nabla(\mu_1 - \mu_2), \quad \frac{\partial u_2}{\partial t} = \nabla \cdot (l u_1 u_2) \nabla(\mu_2 - \mu_1).$$

To avoid redundancy, we may consider, say, the first equation in (8) only. *Constitutive assumptions* now determine $\mu_1,\, \mu_2$.

Constitutive assumptions

In Cahn-Hilliard theory (1958), it is assumed that there is a *free energy*, $\mathcal{F}$,

(9) $$\mathcal{F} = \int_\Omega \left\{ \begin{array}{c} \text{homogeneous} \\ \text{free energy} \end{array} + \begin{array}{c} \text{contributions from} \\ \text{spatial gradients} \end{array} \right\} dV,$$

whose Fréchet derivatives, $\frac{\delta \mathcal{F}}{\delta u_1}$, $\frac{\delta \mathcal{F}}{\delta u_2}$, determine μ_1, μ_2, respectively. We assume the *homogeneous free energy* to contain *entropy* and *interaction energy* contributions,

$$\textit{homogeneous free energy} = \frac{\Theta}{2}\{\ln u_1 + \ln u_2\} - \alpha u_1 u_2,$$

and that *the spatial gradient energy contributions* $= \frac{1}{2}\epsilon^2\{|\nabla u_1|^2 + |\nabla u_2|^2\}$.

The degenerate Cahn-Hilliard equation

For notational simplicity, we set $u(x,t) = u_1(x,t)$, and the starting point for our analysis will thus be the Cahn-Hilliard, (1), with

(10) $$M(u) = M_0(1-u^2), \quad f(u) = \frac{\Theta}{2}\{\ln(1+u) - \ln(1-u)\} - \alpha u,$$

where $f(u) = F'(u)$.

This formulation is in line with the assumptions of Cahn & Hilliard (1958, 1961), and corresponds to a formulation discussed by Elliott & Garcke (1997).

In (10), u represents the difference in the concentrations of the two components, and thus should satisfy $|u(x,\, t)| \leq 1$. For (1),(10), existence, regularity, and invariance of the region $|u| \leq 1$ were proven by Elliott & Garcke (1996). See also Jingxue (1992).

Some distinguished limits...

Setting $x' = (\alpha^{1/2}/\epsilon)x$, $t' = (\alpha^2 M_0/\epsilon^2)t$, and dropping primes,

$$(\text{CH}) \begin{cases} u_t = \nabla \cdot (1-u^2)\nabla[\frac{\theta}{2}\ln[\frac{1+u}{1-u}] - u - \triangle u], & (x,t) \in \Omega_T, \\ n \cdot \nabla u = 0, & (x,t) \in \partial\Omega_T, \\ n \cdot (1-u^2)\nabla[\frac{\theta}{2}\ln[\frac{1+u}{1-u}] - u - \triangle u] = 0, & (x,t) \in \partial\Omega_T, \\ u(x,0) = u_0(x), & x \in \Omega, \end{cases}$$

where $\theta = \Theta/\alpha$ denotes a scaled temperature.

The "shallow quench" limit: $\theta = 1 - \delta$, $x' = (\delta/2)^{1/2}x$, $t' = (\delta^2/4)t$, $u' = (3\delta)^{-1/2}u$, and $\delta \downarrow 0$,

$$u_t + \triangle[2(1-u^2)u + \triangle u] = 0.$$

The "deep quench" limit: let $\theta \to 0$,

$$u_t + \nabla \cdot (1-u^2)\nabla[u + \triangle u] = 0.$$

Existence and regularity

Theorem 1 (Elliott & Garcke, Kohn & Otto,[4]) Let Ω be bounded and convex, $u_0 \in H^1(\Omega)$, and $|u_0| \leq 1$, and let $M(u)$ and $f(u)$ be as prescribed. Then for any $T > 0$, there exists $(u,\, \mathbf{J})$ such that

1. $u \in L^2(0,\, T;\; H^2(\Omega)) \cap L^\infty(0,\, T; H^1(\Omega)) \cap \mathcal{C}([0,\, T];\; L^2(\Omega))$,
2. $u_t \in L^2(0,\, T;\; (H^1(\Omega))')$,
3. $u(0) = u_0$ and $n \cdot \nabla u = 0$ on $\partial\Omega_T := \partial\Omega \times (0,\, T)$,
4. $|u| \leq 1$ a.e. in $\Omega_T := \Omega \times (0,\, T)$,
5. $\mathbf{J} \in L^2(\Omega_T;\, \mathbb{R}^n)$, and $u_t = -\nabla \cdot \mathbf{J}$ in $L^2(0,\, T;\; (H^1(\Omega))')$,
6. $\mathbf{J} = -M(u)\nabla \cdot (-\epsilon^2 \triangle u + f(u))$ in the sense that for all η such that $\eta \in L^2(0,\, T;\; H^1(\Omega,\, \mathbb{R}^n)) \cap L^\infty(\Omega_T; \mathbb{R}^n)$ and $\eta \cdot u = 0$ on $\partial\Omega_T$,

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

   Moreover, defining $E := \frac{1}{2|\Omega|}\int_\Omega \{\int^u f(s)\, ds + |\nabla u|^2\}\, dx$, then for a.e. $t_1 < t_2$, $t_1,\, t_2 \in [0,\, T]$,

7. $E(t_2) - E(t_1) \leq -\int_{t_1}^{t_2}\int_\Omega \frac{1}{M(u)}|\mathbf{J}|^2\, dx.$

Coarsening

Long time behavior of the Cahn-Hilliard equation:

$$u_t = \nabla \cdot (1-u^2)\nabla\left[\frac{\Theta}{2}\{\ln(1+u) - \ln(1-u)\} - \alpha u - \epsilon^2 \triangle u\right],$$

is marked by *coarsening*. During coarsening, phase separated *domains* in which $u(x,t) \approx u_{\pm}$, the "equilibrium phases," *grow* in overall size. Rigorous *upper bounds* for coarsening rates, such as $t^{1/3}$ and $t^{1/4}$, were given by Kohn & Otto in 2002.

We extend their approach, taking into account *temperature* and *mean concentration* dependence, and treating *general convex domains*. We demonstrate that *time* and *temperature* and *mean concentration* transitions may occur.

Upper bounds for coarsening

Kohn & Otto (2002), assuming periodic boundary conditions and $\bar{u} := \frac{1}{\Omega}\int_\Omega u_0(x)\,dx = 0$, obtained the upper bound $l(t) \propto t^{1/3}$ for the dominant length scale, $l(t)$, during coarsening for the "shallow quench limit:"

(11)
$$\begin{cases} u_t + \triangle[2(1-u^2)u + \triangle u] = 0, & (x,t) \in \Omega_T, \\ u(x,0) = u_0(x), & x \in \Omega, \end{cases}$$

and the upper bound $l(t) \propto t^{1/4}$ for the "deep quench limit,"

(12)
$$\begin{cases} u_t + \nabla \cdot (1-u^2)\nabla[u + \triangle u] = 0, & (x,t) \in \Omega_T, \\ u(x,0) = u_0(x), & x \in \Omega. \end{cases}$$

Upper bounds . . .

They defined two length scales,

$1)$ E^{-1}, where E is a scaled free energy

$2)$ and L, where L is the $(W^{1,\infty})^*$ norm of u,

and proved that there exist constants, C_α, such that

(13) $$\frac{1}{T}\int_0^T E^{\theta r} L^{-(1-\theta)r}\, dt \geq C_\alpha T^{-\frac{r}{3}},$$

where $r < 3 + \alpha$, $\theta r > 1$, $(1-\theta)r < 2$, if $L^3(0) \gg 1 \gg E(0)$ and $T \gg L^3(0)$, where $\alpha = 0$ for (11) and $\alpha = 1$ for (12).

Similar analyzes have appeared for *phase field models*, *epitaxial growth*, *Oswald ripening*, and more.

Three lemmas:

Their analysis relied on three lemmas which, generalized to hold for (1), may be stated as follows:

Lemma 1 If $0 < \theta < 1$ and $u_- < \bar{u} < u_+$, then for $t \geq 0$,

$$1 \leq \mathcal{A} + \min\{\mathcal{B}_1, \mathcal{B}_2\},$$

where

$$\mathcal{A} = \frac{2^{5/2}}{(u_\pm^2 - \bar{u}^2)} \left[\left(\frac{(5/u_+)}{[\theta(\frac{1}{6} + h_{\min})]^{1/2}} E(t) + 3\frac{|\partial\Omega|}{|\Omega|} \right) L(t) \right]^{1/2},$$

and

$$\mathcal{B}_1 = \frac{1}{(u_\pm^2 - \bar{u}^2)} \left[\frac{2E(t)}{\theta(\frac{1}{6} + h_{\min})} \right]^{1/2}, \quad \mathcal{B}_2 = \frac{2}{(u_\pm^2 - \bar{u}^2)} [E(t) + \theta \ln 2],$$

where $h_{\min} = h_{\min}(u_\pm)$.

Three lemmas...

Lemma 2 If $u(x,t)$ is a solution of (CH), and $0 < \theta < 1$ and $|\bar{u}| < 1$, then for $t \geq 0$,

(14) $$|\dot{L}|^2 \leq -(1 - u_\pm^2)\dot{E} - (u_\pm^2 - \bar{u}^2)\min\{\mathcal{B}_1, \mathcal{B}_2\}\dot{E}.$$

Lemma 3 Suppose that $|\dot{L}|^2 \leq -AE^\alpha \dot{E}$, $0 \leq t \leq T$, $\alpha = 0, \frac{1}{2}$, or 1.

$i)$ If, moreover, $LE \geq B \quad 0 \leq t \leq T$, then

$$\frac{1}{T}\left[\int_0^T E^{\,r\varphi} L^{-(1-\varphi)\,r}\, dt + L(0)^{(3+\alpha)-r}\right] \geq \vartheta_1 T^{-\frac{r}{(3+\alpha)}}.$$

$ii)$ If, moreover, $E \geq C \quad 0 \leq t \leq T$, then

$$\frac{1}{T}\left[\int_0^T E^{\,\varphi r} L^{-(1-\varphi)\,r}\, dt + L(0)^{2-(1-\varphi)r}\right] \geq \vartheta_2 T^{-\frac{(1-\varphi)r}{2}},$$

where $\vartheta_1 = \vartheta_1(A, B, \alpha, r, \varphi), \quad \vartheta_2 = \vartheta_2(A, C, \alpha, r, \varphi)$.

The predictions of the Lemmas

Identifying $\min\{\mathcal{B}_1, \mathcal{B}_2\}$ determines the tighter bounds in Lemmas 1 and 2. For simplicity, assume boundary contributions to be negligible.

Suppose that $\mathcal{B}_1 = \min\{\mathcal{B}_1, \mathcal{B}_2\}$.

If

$$\mathcal{B}_1 < 1/2, \tag{15}$$

Lemma 1 implies a bound of the form $EL \geq B$, and if $\mathcal{B}_1 > 1/2$, a bound of the form $E \geq C$ is implied.

If, moreover,

$$(u_\pm^2 - \bar{u}^2)\mathcal{B}_1 < (1 - u_\pm^2), \tag{16}$$

Lemma 2 provides an estimate of the form (14) with $\alpha = 0$ and if (16) holds with the opposite sign, an estimate of the form (14) is obtained with $\alpha = 1/2$.

Obtaining coarsening rates...

Suppose $\mathcal{B}_2 = \min\{\mathcal{B}_1, \mathcal{B}_2\}$.

If

(17) $$\mathcal{B}_2 < 1/2,$$

then Lemma 1 implies a bound of the form $EL \geq B$,

and if (17) holds with the opposite sign, then a bound of the form $E \geq C$ is attained.

If, moreover,

(18) $$2E < (1 - u_{\pm}^2) + 2\theta \ln 2,$$

then Lemma 2 implies an estimate of the form (14) with $\alpha = 0$ and if (18) holds with the opposite sign, then an estimate of the form (14) is obtained with $\alpha = 1$.

Obtaining coarsening rates...

Since for any $t \geq 0$, $E(t)$, $L(t)$ are defined, $\min\{\mathcal{B}_1, \mathcal{B}_2\}$ is given by $\mathcal{B}_1$ or $\mathcal{B}_2$, and (15)-(18) hold with one sign or the other, Lemma 3 and the autonomy of (14) imply

Theorem 2 Let $u(x, t)$ be a solution to (CH) such that $u_- < \bar{u} < u_+$ and $0 < \theta < 1$, then neglecting boundary effects, at any given time $t \geq 0$, upper bounds of the form

(19) $$\frac{1}{t - T_1}\left[\int_{T_1}^{t} E^{r\varphi} L^{-(1-\varphi)\,r}\,dt + L(T_1)^{(3+\alpha)-r}\right] \geq \vartheta_1 (t - T_1)^{-\frac{r}{(3+\alpha)}},$$

or

(20) $$\frac{1}{t - T_2}\left[\int_{T_2}^{t} E^{\varphi r} L^{-(1-\varphi)\,r}\,dt + L(T_2)^{2-(1-\varphi)r}\right] \geq \vartheta_2 (t - T_2)^{-\frac{(1-\varphi)r}{2}},$$

hold for appropriate values of the parameters.

Implications

To understand the implications of Lemmas 1-3, we distinguish various parameter regions. It is easy to check that

$(a)\ \min\{\mathcal{B}_1, \mathcal{B}_2\} = \mathcal{B}_1$ when $0 < E < E_-$ or $E > E_+$,
$(b)\ \min\{\mathcal{B}_1, \mathcal{B}_2\} = \mathcal{B}_2$ when $E_- < E < E_+$,

where $E_\pm = ([1-(4\ln 2)\theta\Psi \pm \sqrt{1-(8\ln 2)\theta\Psi}])/(4\Psi)$, $\Psi := \theta[\frac{1}{6} + h_{\min}]$. Note that θ, Ψ, $E_\pm$ can all be expressed as functions of $u_\pm$.

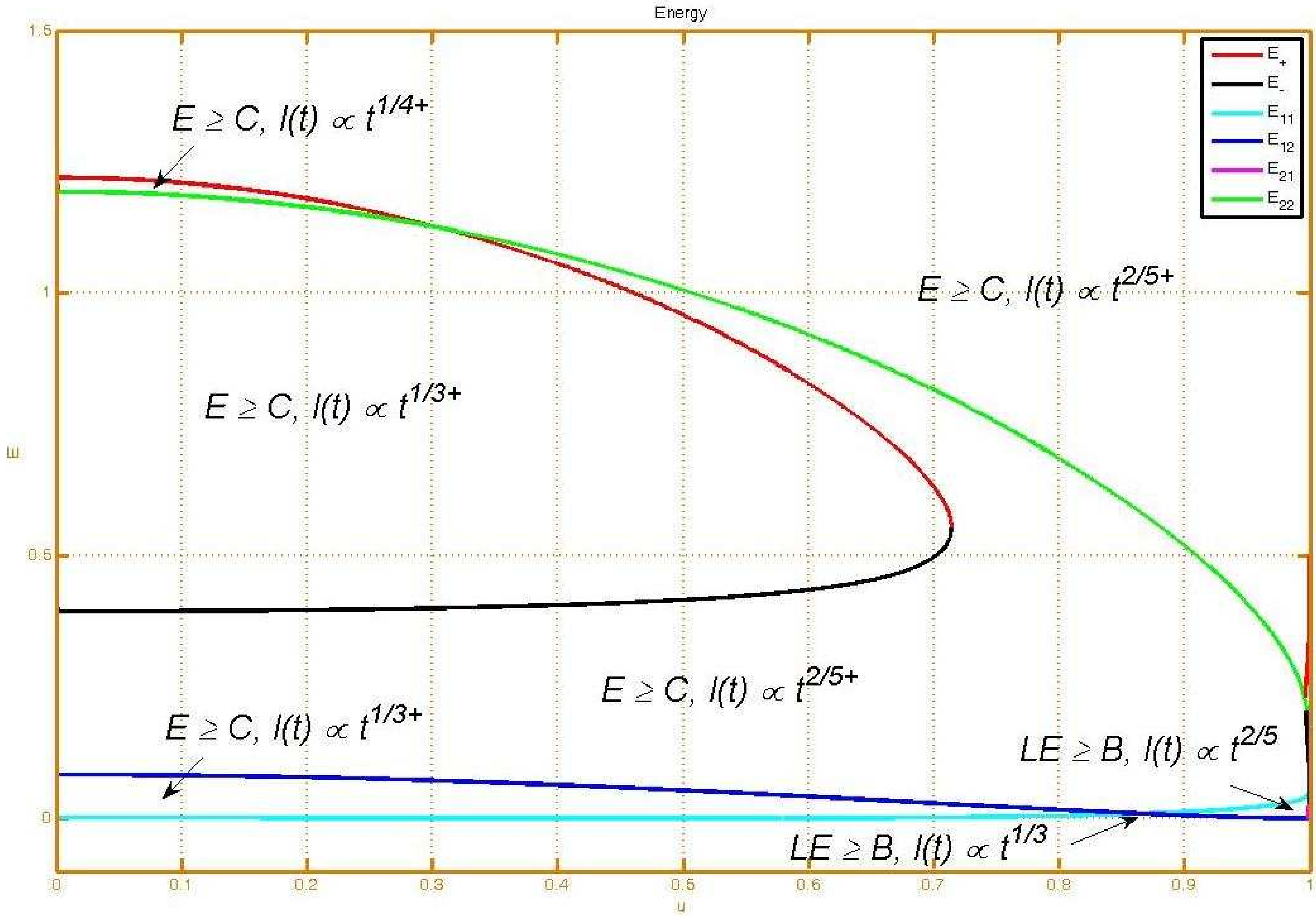
In case (a), (15) holds iff $E < E_{11} := \frac{1}{8}u_\pm^4\Psi(1-\beta^2)^2$,the criterion for the $\alpha = 1/2$ rather than $\alpha = 0$ in (14) when $E > E_{12} := \frac{1}{2}\Psi(1-u_\pm^2)^2$.

In case (b), then (17) holds iff $E < E_{21} := \frac{u_\pm^2}{4}(1-\beta^2) - \theta\ln 2$, where $\beta^2 := \bar{u}^2/u_\pm^2 < 1$, and $\alpha = 1$ rather than $\alpha = 0$ in (14) when $E > E_{22} := \frac{1}{2}(1-u_\pm^2) + \theta\ln 2$.

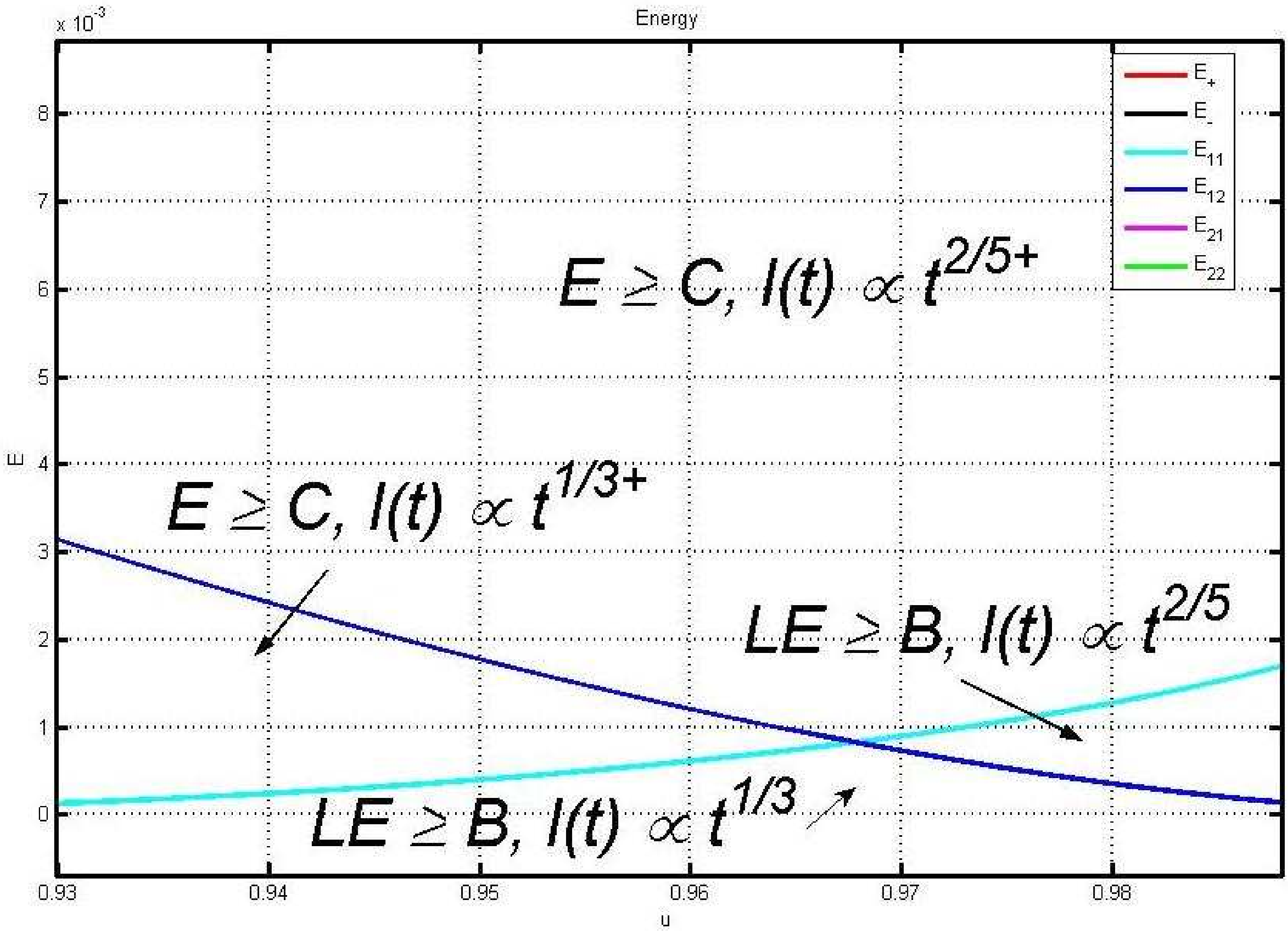
While the bounds and estimates which have been outlined are all quite rigorous, a complete analysis is quite involved ...

In the meantime, some diagrams of energy levels and the implied upper bounds (M. Gruzd & J. Rashed)

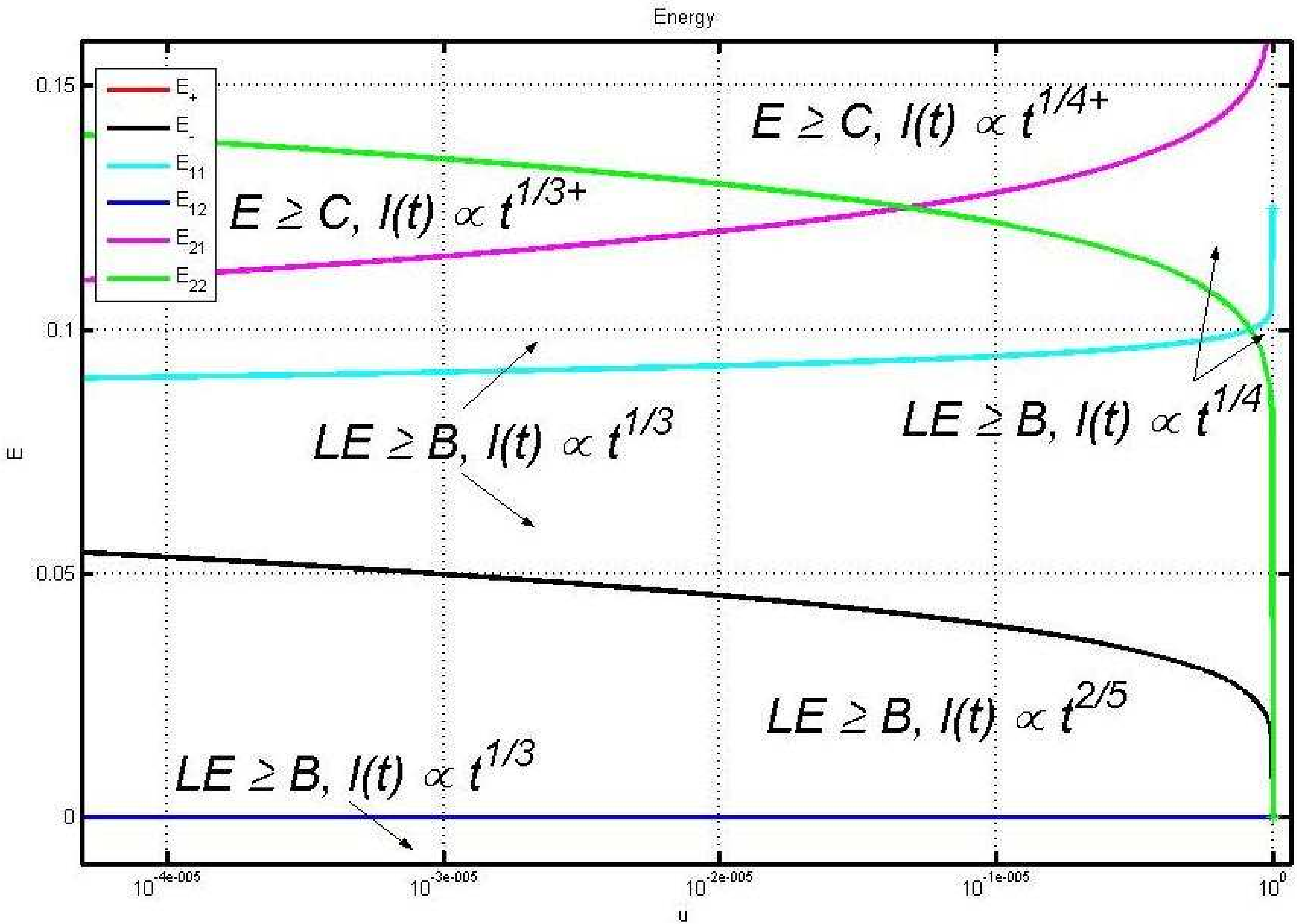
1. Energy levels and upper bounds ...



2. Energy levels and upper bounds ...



3. Energy levels and upper bounds ...



Some further questions ....

- Are *upper bounds* implied for all $t > 0$? Do *some temporal gaps* occur in the upper bounds?
- Is there some *waiting time* for the upper bounds to hold?
- Can the *coefficients* for the upper bounds be calculated?
- Can the *transition times* be calculated or predicted?
- Is $E(0)$ readily calculable and predictable?
- Can the predictions be *correlated* with numerical calculations and experiment?

Various answers and partial answers have been given within the context of the *deep quench obstacle problem*, and the results carry over readily to the Cahn-Hilliard context [6].

Various numerical calculations checking the predictions are planned or in progress [1].

References

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Thank you for your interest!