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THE CAHN-HILLIARD MODEL FOR THE KINETICS OF PHASE SEPARATION

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1 – Introduction

In this paper we consider the Cahn-Hilliard mathematical continuum model of spinodal decomposition (or phase separation) of a binary alloy. The phenomenological model is derived in section one. The existence theory for the Cahn-Hilliard equation is reviewed in section two. Various aspects and generalizations are surveyed in section three. A finite element approximation is studied in section four and, in particular, two fully discrete schemes are shown to possess Lyapunov functionals. Finally in section five some numerical simulations are described.

Consider a binary alloy, comprising of species **A** and **B**, existing in a state of isothermal equilibrium at a temperature, T_m, greater than the critical temperature T_c. The alloy's composition is spatially uniform with the concentration, u, of **B** taking the constant value u_m. Suppose that the alloy is now quenched (rapid reduction of temperature) to a uniform temperature T_m less than T_c. Phase separation takes place in which the composition of the alloy changes from the uniform mixed state to that of a spatially separated two phase structure, each phase being characterised by a different concentration value which is either u_a or u_b.

A phenomenological theory describing this is provided by consideration of a coarse grained Gibb's free energy $\psi(u,T)$ which is such that for $T > T_c$, $\psi_{uu}(u,T) > 0$ and for $T < T_c$, $\psi_{uu}(u,T) < 0$ in just one interval $[u_a^s, u_b^s]$ called the spinodal interval as shown in Figure 1. Associated with this description is the phase diagram which is depicted schematically in Figure 2. The spinodal curve β is the locus of points where $\psi_{uu}(u, T) = 0$. Above the coexistence curve, α, any uniform concentration is stable. Below the spinodal line the state (u_m, T_m) is unstable and the alloy separates into two phases characterised by the values u_a and u_b where the line $T = T_m$ crosses the coexistence curve.

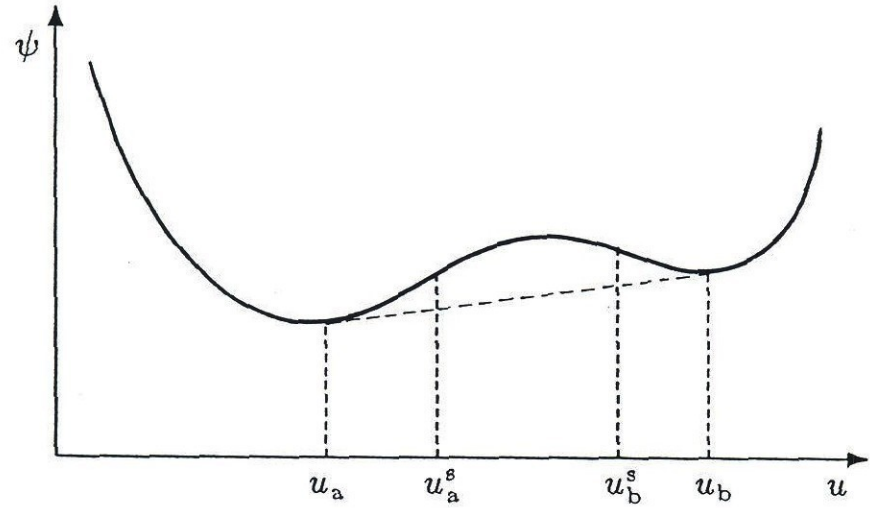

Fig. 1

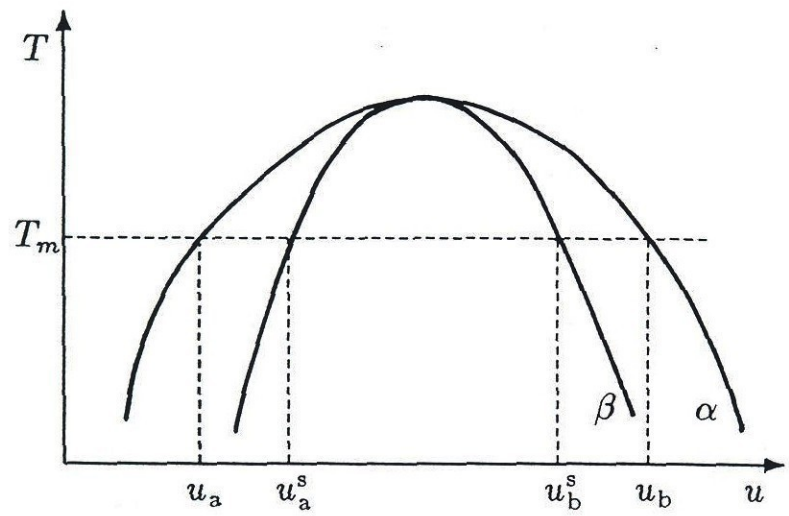

Fig. 2

Suppose that the alloy occupies the spatial domain $\Omega \subset \mathbf{R}^n$ and is isolated. For convenience we suppress the dependence of ψ on T. Given that the mass is fixed, isothermal equilibrium is characterised by minimising the total energy viz

$$\text{(1.1a)} \qquad \min \int_\Omega \psi(u(x))\, dx \quad \text{subject to} \int_\Omega u(x)\, dx = u_m\, |\Omega| \,.$$

Introducing the Lagrange multiplier, μ^*, for the prescribed mass constraint and setting $F(u) = \psi(u) - \mu^*(u - u_m)$ it is clear that (1.1a) is equivalent to

$$\text{(1.1b)} \qquad \min \int_\Omega F(u(x))\, dx \quad \text{subject to} \int_\Omega u(x)\, dx = u_m\, |\Omega| \,.$$

The solution of (1.1b) can now easily be found by choosing a suitable value for μ^*. First consider $T_m > T_c$. In this case set $\mu^* = \psi'(u_m)$ so that $F(u)$ has a unique minimum at $u = u_m$ with $F(u_m) = \psi(u_m)$. Thus the solution of (1.1b) is unique with $u(x) = u_m$, corresponding to a spatially uniform concentration. Now consider $T_m < T_c$. The double well form of $\psi(\cdot)$ implies that there exists two unique values u_{a} and u_{b} defined by

$$\text{(1.2)} \qquad \psi'(u_{\mathrm{a}}) = \psi'(u_{\mathrm{b}}) = \frac{\psi(u_{\mathrm{b}}) - \psi(u_{\mathrm{a}})}{u_{\mathrm{b}} - u_{\mathrm{a}}} \,.$$

Suppose that $u_{\mathrm{a}} \le u_m \le u_{\mathrm{b}}$ and set $\mu^* = (\psi(u_{\mathrm{b}}) - \psi(u_{\mathrm{a}}))/(u_{\mathrm{b}} - u_{\mathrm{a}})$. It follows that $F(\cdot)$ has two absolute minima at $u = u_{\mathrm{a}}$ and $u = u_{\mathrm{b}}$ with $F(u_{\mathrm{a}}) = F(u_{\mathrm{b}})$ and equilibrium configurations consist of

$$\text{(1.3a)} \qquad u(x) = \begin{cases} u_{\mathrm{a}}, & x \in \Omega_{\mathrm{a}} \\ u_{\mathrm{b}}, & x \in \Omega_{\mathrm{b}} \,, \end{cases}$$

where $\overline{\Omega} = \overline{\Omega}_{\mathrm{a}} \cup \overline{\Omega}_{\mathrm{b}}$ such that

$$\text{(1.3b)} \qquad u_{\mathrm{a}}\, |\Omega_{\mathrm{a}}| + u_{\mathrm{b}}\, |\Omega_{\mathrm{b}}| = u_m\, |\Omega_m| \,.$$

Note that for $u_m \notin [u_{\mathrm{a}}, u_{\mathrm{b}}]$ equation (1.3b) cannot be satisfied. For $u_m > u_{\mathrm{b}}$ ($u_m < u_{\mathrm{a}}$) we set $\mu^* = \psi'(u_m)$ and observe that $F(\cdot)$ can have at most two minima at $u = u_m, \hat{u}_m$ with $u_m > \hat{u}_m$. Since the mean value of the concentration is u_m it follows that the equilibrium configuration consists of the homogeneous composition $u = u_m$.

We have just shown that the phase diagram Figure 2 can be explained by thermodynamics in terms of the minimisation of the free energy (1.1a). It is a natural wish to model the evolution of an alloy initially in equilibrium in the uniform state (u_m, T_I) with $T_I > T_c$ which is quenched to a uniform state (u_m, T_m) which lies in the spinodal region. This new state is not in equilibrium and in particular, as the above equilibrium theory predicts, the alloy separates into two phases lying on the coexistence curve. The kinetics of phase separation can be modelled using non-equilibrium thermodynamics. We assume that the system is isothermal. The mass flux is postulated to be (DeGroot and Mazur [12])

$$\mathbf{J} = -M\,\nabla\mu\ , \tag{1.4}$$

where $M > 0$ denotes the *mobility* and μ the *chemical potential* difference between the species **A** and **B** which satisfies

$$\mu = \psi'(u)\ . \tag{1.5}$$

This leads to Fick's law of diffusion

$$\mathbf{J} = -M\,\psi''(u)\,\nabla u \tag{1.6}$$

and the mass balance law

$$\frac{d}{dt}\int_{\mathcal{R}} u = -\int_{\partial\mathcal{R}} \mathbf{J}\cdot\mathbf{n}, \quad \text{for } \mathcal{R}\subset\Omega\ , \tag{1.7}$$

yields the diffusion equation

$$\frac{\partial u}{\partial t} = \nabla(K(u)\,\nabla u)\ , \tag{1.8}$$

where the *diffusivity* $K(u) = M\,\psi''(u)$.

In order to check that (1.4) is consistent with the second law of thermodynamics which for isothermal diffusion in a binary system is (DeGroot and Mazur [12])

$$\frac{d}{dt}\int_{\mathcal{R}} TS + \int_{\partial\mathcal{R}}(-\mu\mathbf{J}\cdot\mathbf{n}) \geq 0, \quad \text{for } \mathcal{R}\subset\Omega\ , \tag{1.9}$$

we note that $\psi = e - TS$, where e is the bulk internal energy and S is the entropy. Since $de/dt = 0$ it follows that (1.9) becomes

$$\frac{d}{dt}\int_{\mathcal{R}} \psi + \int_{\partial\mathcal{R}} \mu\,\mathbf{J}\cdot\mathrm{n} \leq 0\,, \tag{1.10}$$

or

$$\frac{\partial\psi}{\partial t} + \nabla(\mu\,\mathbf{J}) \leq 0, \qquad \text{a.e. } \Omega\,.$$

Since the left-hand side of the above inequality is equal to

$$\mu\,u_t + \mu\,\nabla\cdot\mathbf{J} + \nabla\mu\cdot\mathbf{J} = -M\,|\nabla\mu|^2\,.$$

We see that (1.4) and (1.5) are consistent with the mass balance law and (1.9).

The above development has two obvious drawbacks for $T_m < T_c$. First, the equilibrium theory predicts any decomposition of Ω into two phases as long as (1.3b) holds and this allows a continuum of equilibrium configurations with complex interface morphology and in particular interfaces between the phases with arbitrarily large measure. Second, the diffusion coefficient $K(u)$ is uniformly positive for $T_m > T_c$ but for $T_m < T_c$, $K(u)$ is negative in the spinodal interval. Hence the mass balance equation allows forward and backward diffusion and the initial value problem is classically not well posed from the mathematical point of view.

In order to model surface energy of the interface separating the phases (also known as capillarity) Cahn and Hilliard [7] modify the free energy by adding the gradient term $\gamma|\nabla u|^2/2$ where $\gamma > 0$ so that the free energy becomes

$$\Psi = \psi(u) + \frac{\gamma}{2}\,|\nabla u|^2 \tag{1.11}$$

and $\psi(\cdot)$ is called the homogeneous free energy. Gradients had previously been used to model capillarity by van der Waals [53]. We refer also to Hillert [29] where a discrete version was developed. The Cahn-Hilliard-van der Waals model for the equilibrium description of phase separation is thus to

$$\min\int_\Omega \{\psi(u(x)) + \frac{\gamma}{2}\,|\nabla u|^2\}\,dx, \quad \text{subject to} \int_\Omega u(x)\,dx = u_m\,|\Omega|. \tag{1.12}$$

It is convenient to introduce the generalised chemical potential w,

$$w = \psi'(u) - \gamma \Delta u , \tag{1.13}$$

so that w is the functional derivative of the energy

$$\mathcal{E}(u) = \int_\Omega \left\{ \psi(u) + \frac{\gamma}{2} |\nabla u|^2 \right\} dx , \tag{1.14}$$

i.e.,

$$\langle w, v \rangle = \langle \mathcal{E}'(u), v \rangle \equiv (\psi'(u), v) + \gamma(\nabla u, \nabla v) ,$$

where $(\cdot,\cdot)$ denotes the $L^2(\Omega)$ inner-product.

The mass flux is again given by (1.4) so that the generalised diffusion equation for this non-equilibrium gradient theory of phase separation is, Cahn [5],

$$\frac{\partial u}{\partial t} = (\nabla M \nabla w) = \nabla \Big(M \nabla (\psi'(u) - \gamma \Delta u) \Big) . \tag{1.15}$$

This fourth order in space, nonlinear time dependent partial differential equation is called the Cahn-Hilliard equation. For a closed system there is no mass flux so that

$$M \nabla w \cdot \mathbf{n} = 0 \quad \text{on } \partial\Omega \tag{1.16a}$$

and for the other free boundary condition we take the natural boundary condition associated with the variational problem (1.12)

$$\gamma \nabla u \cdot \mathbf{n} = 0 \quad \text{on } \partial\Omega . \tag{1.16b}$$

The initial boundary-value problem for a closed system is then to solve (1.15) subject to the boundary conditions (1.16) and the initial condition

$$u(x,0) = u_0(x) , \quad x \in \Omega . \tag{1.17}$$

The form of $u_0(x)$ which is of interest in modelling the quenching process described earlier is

$$u_0(x) = u_m + \epsilon(x), \quad \int_\Omega \epsilon(x)\, dx = 0 , \quad |\epsilon(x)| \ll 1 . \tag{1.18}$$

Other boundary conditions which are of interest are:

Dirichlet conditions.

$$u(x) = u_g(x), \quad w = w_g(x), \quad x \in \partial\Omega \,. \tag{1.19}$$

Periodic conditions. $\Omega = (0, L)^n$

$$\mathrm{D}^j u|_{x_i=0} = \mathrm{D}^j u|_{x_i=L}, \quad i = 1, \ldots, n, \; j = 0, \ldots, 3 \,. \tag{1.20}$$

We remark that the second law of thermodynamics becomes, for any open $\mathcal{R} \subset \Omega$

$$\frac{d}{dt}\int_{\mathcal{R}} \left\{ \psi(u) + \frac{\gamma}{2}|\nabla u|^2 \right\} + \int_{\partial \mathcal{R}} w\, \mathbf{J} \cdot \mathbf{n} \leq 0 \tag{1.21}$$

and since the left hand side of (1.21) is

$$\int_{\mathcal{R}} u_t w + \int_{\partial \mathcal{R}} u_t \gamma \nabla u \cdot \mathbf{n} - \int_{\mathcal{R}} \nabla(w M \nabla w) \,,$$

inequality (1.21) holds for u solving (1.15) and any of (1.16), (1.19) or (1.20). For an interesting rational non-equilibrium thermodynamics theory of phase separation and capillarity we refer to Gurtin [27].

Observe that, in the case of Neumann and periodic boundary conditions, the solution to the initial value problem satisfies

$$\frac{d\mathcal{E}(u)}{dt} = \int_\Omega [\psi'(u)\, u_t + \nabla u \, \nabla u_t]\, dx = (w, u_t) = -\int_\Omega |\nabla w|^2 \, dx \tag{1.22a}$$

$$\frac{d}{dt}\int_\Omega u \, dx = 0 \,, \quad \int_\Omega u(x,t)\, dx = \int_\Omega u_0 \, dx \tag{1.22b}$$

and, for the Dirichlet problem, with

$$\mathcal{E}_{\mathrm{D}}(u) \equiv \mathcal{E}(u) - (w_g, u) \tag{1.23a}$$

$$\frac{d}{dt}\mathcal{E}_{\mathrm{D}}(u) = (w - w_g, u_t) = -\int_\Omega |\nabla(w - w_g)|^2 \, dx \,, \tag{1.23b}$$

where w_g is defined in Ω to be harmonic.

This is in accordance with the requirement for this model of kinetics of phase separation that the evolution of a non-equilibrium composition is to a composition of lower energy. Indeed it is a natural question to ask if the time dependent solution to the initial value problem converges to a minimiser of the energy as $t \to \infty$.

The simplest form of ψ which has a double well is

$$\psi(u) = \frac{1}{4}(u^2 - \beta^2)^2 \tag{1.24a}$$

$$\phi(u) \equiv \psi'(u) = u\,(u^2 - \beta^2)\,, \qquad \psi''(u) = 3\,u^2 - \beta^2\,, \tag{1.24b}$$

so that the spinodal interval is $[-\beta/\sqrt{(3)}, +\beta/\sqrt{(3)}]$ and $u_a = -\beta$, $u_b = +\beta$. In the mathematical analysis of section 2 and section 4 we take ψ to be of this form and the mobility $M = 1$.

Reviews of spinodal decomposition and the Cahn-Hilliard model may be found in Hilliard [30], Cahn and Hilliard [8], Skripov and Skripov [50], Gunton and Droz [23], Gunton, San-Miguel and Sahni [24], Koch [34], Novick-Cohen and Segel [42] and Penrose [45].

2 – Existence Theory

Let Ω be a bounded domain in $\mathbf{R}^n$ $(n \le 3)$ with a Lipschitz boundary. Let $\psi(\cdot)$ be defined by (1.24). Global existence of a solution to the initial boundary value problem (1.15, 1.16, 1.17) i.e. $u \in L^\infty(0,T;H^1(\Omega))$, $w \in L^2(0,T;H^1(\Omega))$ and $du/dt \in L^2(0,T;(H^1(\Omega))')$ such that

$$\Big(\frac{\partial u}{\partial t}, \eta\Big) + (\nabla w, \nabla \eta) = 0\,, \qquad \forall \eta \in H^1(\Omega) \tag{2.1a}$$

$$\gamma(\nabla u, \nabla \eta) + (\phi(u), \eta) = (w, \eta)\,, \qquad \forall \eta \in H^1(\Omega) \tag{2.1b}$$

$$u(0) = u_0 \in H^1(\Omega) \tag{2.1c}$$

is an immediate consequence of the fact that $\mathcal{E}(u)$ is a Lyapunov functional, see (1.22a),

$$\mathcal{E}(u) + \int_0^t |w|_1^2\, d\tau = \mathcal{E}(u_0)\,, \tag{2.2}$$

with $|\cdot|_j \equiv \|D^j \cdot\|_{L^2(\Omega)}$; where we also take advantage of the non-negativity of ψ, that $L^4 \hookrightarrow H^1(\Omega)$ and that $(u-u_0,1)=0$. This can be made rigorous by appropriate use of a Faedo-Galerkin method. Similar considerations apply to the cases of periodic conditions and Dirichlet boundary conditions. Existence of a more regular solution is proved in Elliott and Zheng [21] and Nicolaenko and Scheurer [40]. See also Nicolaenko, Scheurer and Témam [39] where a more general polynomial form of ψ is assumed and periodic boundary conditions for $n \leq 3$ and Neumann conditions for $n=1$ are considered. The tool for obtaining estimates on higher order derivatives is Sobolev interpolation inequalities. We show here how some estimates may be obtained in a more direct way.

For convenience let $\partial\Omega \in C^\infty$. Set $\{e_j\}$ to be the eigenfunctions

$$-\Delta e_j + e_j = \lambda_j e_j\,, \qquad x \in \Omega, \quad \frac{\partial e_j}{\partial \nu} = 0 \text{ on } \partial\Omega\,, \tag{2.3}$$

so that $e_j \in C^\infty(\overline{\Omega})$, $\{e_j\}$ is an orthonormal basis for $L^2(\Omega)$ and $\{e_i\}$ is an orthogonal basis for $H^1(\Omega)$ with $(e_i,e_j)_{H^1(\Omega)} = \lambda_i \delta_{ij}$. Note that $e_1 = 1/|\Omega|^{1/2}$. Set V^m to be the span $\{e_j\}_{j=1}^m$. The Galerkin approximation for the Neumann case is: Find $\{u_m, w_m\} \in V^m \times V^m$ such that

$$\Big(\frac{du_m}{dt}, e_i\Big) = (\Delta w_m, e_i)\,, \qquad i = 1,2,\ldots,m \tag{2.4a}$$

$$(w_m, e_i) = \gamma(\nabla u_m, \nabla e_i) + (\phi(u_m), e_i)\,, \qquad i = 1,2,\ldots,m \tag{2.4b}$$

$$u_m(0) = P^m u_0\,, \tag{2.4c}$$

where P^m is the projection defined by

$$P^m v = \sum_{j=1}^m (v, e_j)\, e_j = \sum_{j=1}^m \Big(v, \frac{e_j}{\sqrt{\lambda_j}}\Big)_{H^1} \frac{e_j}{\sqrt{\lambda_j}} \tag{2.5a}$$

and

$$\|P^m\|_{\mathcal{L}(H^1,V^m)} = \|P^m\|_{\mathcal{L}(L^2,V^m)} = 1\,. \tag{2.5b}$$

Clearly (2.4) is a system of first order ordinary differential equations for the coefficients of $u_m = \sum_j c_j e_j$ and thus (2.4) has a unique solution local in time. Note that

$$\psi(u) = \frac{1}{8} u^4 + \frac{1}{8} (u^2 - 2\beta^2)^2 - \frac{1}{4}\beta^4$$

so that

$$\frac{1}{8} u^4 - \frac{1}{4}\beta^4 \le \psi(u) \le \frac{1}{4} u^4 + \frac{1}{4}\beta^2 . \tag{2.6}$$

Therefore from the fact that, as in (1.22a),

$$\frac{d}{dt}\mathcal{E}(u_m) = -|w_m|_1^2 ,$$

we obtain the estimate

$$\frac{\gamma}{2}|u_m(t)|_1^2 + \frac{1}{8}\|u_m(t)\|_{L^4}^4 + \int_0^t |w_m(\tau)|_1^2 \, d\tau \le \tag{2.7}$$

$$\le \frac{\beta^2}{2} + \frac{\gamma}{2}|u_m(0)|_1^2 + \frac{1}{4}\|u_m(0)\|_{L^4}^4 \le C .$$

Bearing in mind the convergence properties of $P^m u_0$ to u_0 in $H^1(\Omega)$ we obtain from (2.7) an estimate of the left hand side uniform in m and t. We use C generically to denote a constant independent of m and t.

It is easy to see that

$$w_m = -\gamma \Delta u_m + P^m \phi(u_m) . \tag{2.8}$$

Hence the following hold

$$\frac{dw_m}{dt} = -\gamma \Delta \frac{du_m}{dt} + P^m \left[\phi'(u_m)\frac{du_m}{dt}\right] \tag{2.9a}$$

$$\frac{du_m}{dt} = \Delta w_m , \qquad \frac{d\nabla u_m}{dt} = \nabla \Delta w_m . \tag{2.9b}$$

Multiplying (2.9a) by $du_m/dt \in V^m$ and integrating we obtain

$$\left(\frac{dw_m}{dt}, \frac{du_m}{dt}\right) = \gamma \left|\frac{du_m}{dt}\right|_1^2 + \left(\phi'(u_m)\frac{du_m}{dt}, \frac{du_m}{dt}\right)$$

and since $dw_m/dt \in V^m$, we obtain from (2.9b) that

$$\left(\frac{dw_m}{dt}, \frac{du_m}{dt}\right) = -\frac{1}{2}\frac{d}{dt}|w_m|_1^2 \ ;$$

therefore the following equation

$$\frac{1}{2}\frac{d}{dt}|w_m|_1^2 + \gamma\,|\Delta w_m|_1^2 + 3\,(u_m^2\,\Delta w_m, \Delta w_m) = \beta^2\,|\Delta w_m|_0$$
$$= -\beta^2\,(\nabla w_m, \nabla\Delta w_m)$$

holds. Hence we obtain the estimate

$$(2.10)\quad |w_m(t)|_1^2 + \gamma\int_0^t |\Delta w_m(\tau)|_1^2\,d\tau \le |w_m(0)|_1^2 + \frac{\beta^4}{\gamma}\int_0^t |w_m(\tau)|_1^2\,d\tau \ .$$

In order to estimate $|w_m(0)|_1$ we assume that

$$(2.11)\qquad \Delta u_0 \in H^1(\Omega) \quad \text{and} \quad \frac{\partial u_0}{\partial\nu} = 0 \ \text{ on } \partial\Omega \ .$$

It follows that

$$(2.12a)\qquad P^m\,\Delta u_0 = \Delta P^m\,u_0$$

and, in $H^1(\Omega)$,

$$(2.12b)\qquad \lim_{m\to\infty}\Delta u_m(0) \equiv \lim_{m\to\infty}\Delta P^m\,u_0 = \lim_{m\to\infty}P^m\,\Delta u_0 = \Delta u_0 \ .$$

It follows from (2.4b) that

$$|w_m|_1^2 = (w_m, -\Delta w_m) = \gamma(\nabla\Delta u_m, \nabla w_m) + (\phi'(u_m)\,\nabla u_m, \nabla w_m) \ ,$$

yielding

$$|w_m(0)|_1 \le \gamma\,|\Delta u_m(0)|_1 + \|\phi'(u_m(0))\|_{L^\infty}\,|u_m(0)|_1 \ .$$

Hence we obtain from (2.10) and (2.7) that

$$(2.13)\qquad |w_m(t)|_1^2 + \gamma\int_0^t |\Delta w_m(\tau)|_1^2\,d\tau \le C \ .$$

Since

$$(w_m, 1) = (\phi(u_m), 1) \leq \beta^2 \|u_m\|_{L^1} + \|u_m\|_{L^3}^3 ,$$

it follows from the Poincaré inequality

$$|v|_0 \leq C\left[|v|_1 + |(v,1)|\right], \quad \forall v \in H^1(\Omega) , \tag{2.14}$$

that

$$\|w_m(t)\|_{H^1} + \int_0^t |\Delta w_m(\tau)|_1^2 \, d\tau \leq C . \tag{2.15}$$

Furthermore (2.8) implies that

$$\gamma |\Delta u_m(t)|_0 \leq |w_m(t)|_0 + |P^m \phi(u_m(t)|_0 ;$$

since

$$|\phi(u_m)|_0 \leq \|u_m\|_{L^6}^6 + \beta^2 |u_m|_0^2$$

and $L^6(\Omega) \hookrightarrow H^1(\Omega)$, $n \leq 3$, it follows that

$$|\Delta u_m(t)|_0 \leq C . \tag{2.16}$$

Finally we observe that

$$\gamma \nabla \Delta u_m = -\nabla w_m + \nabla P^m \phi(u_m) ;$$

since

$$|P^m \phi(u_m)|_1 \leq |\phi(u_m)|_1 \leq 3 \|u_m\|_{L^\infty}^2 |u_m|_1 + \beta^2 |u_m|_1$$

and $L^\infty(\Omega) \hookrightarrow H^2(\Omega)$, $n \leq 3$, it follows that

$$|\Delta u_m(t)|_1 \leq C . \tag{2.17}$$

These estimates imply the existence of a solution to the Cahn-Hilliard equation with initial data $u_0 \in H_E^2(\Omega) = \{v \in H^2(\Omega) : \partial v/\partial \nu = 0 \text{ on } \partial\Omega\}$ and $\Delta u_0 \in H^1(\Omega)$ such that

$$\begin{aligned} &u \in L^\infty(0,T; H^3(\Omega)) \cap C[0,T; H_E^2(\Omega)], \\ &u_t \in L^2(0,T; H^1(\Omega)), \quad w \in L^2(0,T; H^3(\Omega)) , \end{aligned} \tag{2.18}$$

and

$$\|u(t)\|_{H^3(\Omega)} + \|w(t)\|_{H^1(\Omega)} \leq C\,, \qquad \forall t\,. \tag{2.19}$$

3 – Miscellaneous Considerations

3.1. The linear Cahn-Hilliard equation

Setting $u(x,t) = u_m + \epsilon\,\eta(x,t) + ...$ to be the solution of (1.15) we obtain the following approximate linearised equation for η:

$$\eta_t = -\gamma\,\Delta^2\eta + \psi''(u_m)\,\Delta\eta\,, \qquad x \in \Omega\,, \tag{3.1a}$$

$$\frac{\partial\eta}{\partial\nu} = 0, \quad \frac{\partial\Delta\eta}{\partial\nu} = 0\,, \qquad x \in \partial\Omega\,, \tag{3.1b}$$

$$\eta(x,0) = \eta_0(x)\,, \qquad x \in \Omega\,. \tag{3.1c}$$

In one space dimension $\Omega = (0,L)$ a solution is

$$\eta(x,t) = \sum_{k=1}^{\infty} A_k\, e^{-\omega_k t} \cos(k\pi x/L) \tag{3.2a}$$

$$\omega_k = \frac{k^2\,\pi^2}{L^2}\Big(\psi''(u_m) + \frac{\gamma\,k^2}{L^2}\Big)\,. \tag{3.2b}$$

Thus if u_m lies in the spinodal interval and γ is sufficiently small the amplitude of a finite number of long wavelength perturbations will grow exponentially in time; for $k^2 < -L^2\,\psi''(u_m)/\gamma \equiv (k_c)^2$. In particular the maximum growth rate is for the wave number $k = k_c/\sqrt{2}$.

Initial studies of the validity of the Cahn-Hilliard model for spinodal decomposition were based on this linear stability analysis; see Gunton, San-Miguel and Sahni [24] and Gunton and Droz [23] for reviews.

3.2. Asymptotic long time behaviour

The stationary problem associated with (2.1) is: find $\{u^*, w^*\} \in H^1(\Omega) \times \mathbf{R}$ such that

$$-\gamma\,\Delta u^* + \phi(u^*) = w^*\,, \qquad x \in \Omega\,, \tag{3.3a}$$

$$\frac{\partial u^*}{\partial \nu} = 0\,, \qquad x \in \Omega \tag{3.3b}$$

$$\int_\Omega u^*(x)\,dx = \int_\Omega u_0(x)\,dx\,. \tag{3.3c}$$

Clearly u^* is a critical point of $\mathcal{E}(\cdot)$ varying over the set $K = \{v \in H^1(\Omega):\ \int_\Omega v\,dx = \int_\Omega u_0\,dx\}$ and w^* is the Lagrange multiplier associated with the prescribed mass constraint. One solution of (3.3) is

$$u^* = \frac{(u_0, 1)}{|\Omega|} = M\,, \qquad w^* = \phi(M)\,. \tag{3.4}$$

It is easy to see that if $\sqrt{\gamma} > \beta\, C_{\mathrm{p}}$ where C_{p} is the Poincaré constant in (2.14) then the solution is unique. However in general for γ small there will be multiple solutions. In particular Zheng Songmu [55] has shown in one space dimension that if $|M| < \beta$ and ψ is given by (1.24) then there are a finite number of solutions and when $M = 0$ there are $2\,N_0 + 1$ solutions where $N_0 \le \beta\,L/(\pi\,\sqrt{\gamma}) < N_0 + 1$. Explicit formulae for solutions were obtained by Novick-Cohen and Segel [42].

The estimates (2.18, 2.19) obtained in section 2 allow the use of results in continuous dynamical systems, see Témam [52], to make some statements concerning the behaviour of $u(x,t)$ as $t \to \infty$, see Zheng Songmu [55].

Denoting by $S(t)$ the solution operator to the initial value problem (2.1), it follows that $S(t)$ is a continuous nonlinear semigroup and the orbit $\bigcup_{t>0} S(t)\,u_0$ is relatively compact in $H^2_E(\Omega)$. Thus the ω-limit set of u_0,

$$\omega(u_0) = \left\{ v \in H^2_E(\Omega):\ \exists\, t_n \ s.t.\ \lim_{t_n \to \infty} u(t_n) = v \ \text{ in } H^2(\Omega) \right\}\,, \tag{3.5}$$

has the properties

1) $\omega(u_0)$ is compact and connected;

2) $S(t)\,\omega(u_0) \subset \omega(u_0), \quad \forall t \geq 0$;

3) $\mathcal{E}(v)$ is the same constant $\forall v \in \omega(u_0)$;

4) If $v \in \omega(u_0)$ then v solves (3.3).

It follows that if the set of solutions to (3.3) are discrete then $\omega(u_0)$ consists of just one element u^* and

$$\lim_{t \to \infty} u(t) = u^* \ .$$

This is the case in one dimension as explained above.

Much more information concerning the asymptotic behaviour for large t has been obtained by Nicolaenko, Scheurer and Témam [39] (see also Témam [52]). In particular they derive results about the structure of attractors and the inertial manifold.

A detailed formal asymptotic study of the Cahn-Hilliard equation during the later stages of phase separation has been made by Pego [44]. One of the many interesting features of the paper is the derivation of a formal relation between the Cahn-Hilliard equation and the Stefan problem.

3.3. The stochastic Cahn-Hilliard-Cook equation

The theory developed by Cahn [5] and Cahn-Hilliard [7] leading to the nonlinear Cahn-Hilliard equation (1.15) does not take into account thermal fluctuations in composition. The theory of Cook [10] introduces a stochastic source, namely

$$u_t = -\gamma\,\Delta^2 u + \Delta\phi(u) + \xi \ , \tag{3.6a}$$

where

$$\mathbf{E}\Big(\xi(x,t)\,\xi(x',t')\Big) = -\epsilon\,\Delta\delta(x-x')\,\delta(t-t') \ . \tag{3.6b}$$

Langer [35] has also developed a statistical theory of spinodal decomposition leading to a Fokker-Planck equation from which the

Cahn-Hilliard-Cook equation (3.6) can be derived. Equation (3.6a) is known as the 'model B' equation in critical dynamics, Hohenberg and Halperin [31].

An existence theory for the initial value problem associated with (3.6a) and the smoother noise term

$$\mathbf{E}\Big(\xi(x,t)\,\xi(x',t')\Big) = -\epsilon\, k(x,x')\,\delta(t-t') \tag{3.6c}$$

has been developed by Elezovic and Mikelic [15].

Numerical simulations for the stochastic equation (3.6) have been performed by Petschek and Metiu [46], Elder, Rogers and Desai [14] Rogers, Elder and Desai [48] and Milchev, Heermann and Binder [37].

3.4. The limit $\gamma \to 0$: equilibrium

It has been of great interest to mathematicians in recent years to consider the relation between (1.12) and (1.1a). Does the limit as $\gamma \to 0$ of minimisers u_γ of (1.12) select solutions of (1.1a) with 'minimal interface'? Carr, Gurtin and Slemrod [9] studied the one dimensional version of (3.3) and in particular proved that

1) Solutions of (3.3) with more than interface (i.e. non-monotone) are not local minimisers of $\mathcal{E}(\cdot)$;

2) For γ sufficiently small $\mathcal{E}(\cdot)$ has a unique minimiser which has one interface (note that $u(L-x)$ has the same free energy).

More generally, for multidimensions and general ψ, Modica [38] has shown that the limits of minimisers as $\gamma \to 0$ minimise the measure of the interface between the two phases. We refer also to Alikakos and Simpson [1], Sternberg [51], Gurtin [26], Gurtin and Montano [28] and Luckhaus and Modica [36].

A numerical study of the one dimensional steady state problem has been performed by Eilbeck, Furter and Grinfeld [13] who were particularly interested in the implications for the transition between spinodal decomposition and nucleation.

3.5. The limit $\gamma \to 0$: evolution

Nonlinear forward-backward diffusion equations of the form (1.8) will not in general possess classical or even weak solutions. Hőllig [32] and Hőllig and Nohel [33] considered the equation

$$v_t = \phi(v_x)_x \tag{3.7a}$$

$$v_x(0,t) = v_x(1,t) = 0\,, \quad v(x,0) = v_0(x)\,, \tag{3.7b}$$

which is closely related to (1.8)

$$u_t = \phi(u)_{xx} = (\psi''(u).u_x)_x \tag{3.8a}$$

$$u(0,t) = u(1,t) = 0\,, \quad u(x,0) = u_0(x)\,, \tag{3.8b}$$

by $u = v_x$.

Hőllig [32] showed that if $v_0'(x)$ takes values in the spinodal interval then (3.7) has infinitely many weak solutions and if furthermore v_0 is not analytic, then it does not have a solution with v_x being continuous. Numerical experiments, Hőllig and Nohel [33] and Elliott [16], show that certain finite difference approximations of (3.8) display phase separation. It is shown in Elliott [16] that these explicit in time finite difference approximations converge to a 'measure-valued' solution. However one would like more information about the limit. It is natural to consider the limit as $\gamma \to 0$ of solutions to the evolutionary Cahn-Hilliard equation (1.15)

3.6. Other forms of the energy

- In the presence of a gravitational field the energy functional may be modified to, see Shiwa [49],

$$\mathcal{E}(u) = \int_\Omega \Big[\psi(u) + \frac{\gamma}{2}\,|\nabla u|^2 - f\,u\Big]\,dx\,.$$

  This has been studied from the mathematical and numerical point of view by Copetti [in preparation].

– The energy functionals

$$\mathcal{E}(u) = \int_\Omega \big[\psi(u) + \alpha\,|\nabla u|\big]\,dx$$

$$\mathcal{E}(u) = \int_\Omega \Big[\psi(u) + \frac{\gamma}{2}\,|\nabla u|^2 + \alpha\,|\nabla u|\Big]\,dx$$

have been studied by Elliott and Mikelic [20]. The term $\alpha\,|\nabla u|$ can be used to penalise interfacial energy; see also Visintin [54].

– A model suggested in Oono and Puri [43] is to replace the smooth Gibb's free energy $\psi(u)$ by

$$I_K(u) - \frac{1}{2}\,u^2\,,$$

where

$$I_K(u) = \begin{cases} +\infty, & |u| > 1\,, \\ 0, & |u| \le 1\,. \end{cases}$$

This leads to a non-standard parabolic variational inequality which has been studied by Blowey [in preparation].

3.7. Stefan problem with surface tension

The Stefan problem with surface tension for the diffusion of heat in solidification of metals has been modelled by the so called Phase Field equation, Caginalp [3]:

(3.9a) $$\tau\,u_t = \gamma\,\Delta u - \phi(u) + w$$

(3.9b) $$w_t + \lambda\,u_t = K\,\Delta w\,,$$

where w is the temperature and u is a phase or order parameter with u_a and u_b defining the solid and liquid phases. We observe that the Cahn-Hilliard equation is a particular limit of (3.9). The connection between the Cahn-Hilliard equation and the Stefan problem with surface tension has yet to be fully explored. Certainly the coarsening (or Ostwald ripening) of dendritic structures in solidification is similar to the coarsening process in the later stages of spinodal decomposition. We refer also to Gurtin [25], Visintin [54] and Luckhaus and Modica [36]. Caginalp [4] has also proposed replacing (3.9a) by the Cahn-Hilliard equation (1.15) itself.

4 – Numerical Analysis

In this section we shall consider the finite element approximation of the initial value problem:

Find $\{u(x,t), w(x,t)\}$ such that

$$\frac{\partial u}{\partial t} = \Delta w \;, \tag{4.1a}$$

$$w = -\gamma\, \Delta u + \phi(u) + f(x) \;, \tag{4.1b}$$

for $t > 0$ in a bounded domain $\Omega \subset \mathbf{R}^n$ $(n \leq 3)$ subject to the initial and boundary conditions

$$u(x,0) = u_0(x) \,, \qquad x \in \Omega \tag{4.1c}$$

$$\frac{\partial u}{\partial \nu} = \frac{\partial w}{\partial \nu} = 0 \,, \qquad x \in \partial\Omega, \quad t > 0 \;, \tag{4.1d}$$

where $\partial\Omega$ is sufficiently smooth.

For definiteness we assume that $\psi(\cdot)$ is the polynomial of degree 4

$$\psi(r) = \frac{1}{4}\,(r^2 - \beta^2)^2 \;, \tag{4.2a}$$

so that

$$\psi''(r) \geq -\beta^2 \,, \qquad \forall r \;. \tag{4.2b}$$

Let us consider a quasi-uniform family of triangulations $\mathcal{T}^h$ of Ω with boundary elements being allowed to have one curvilinear side so that $\Omega = \bigcup_{\tau \in \mathcal{T}^h} \tau$. Associated with $\mathcal{T}^h$ is the finite element space $S^h \in H^1(\Omega)$

$$S^h = \left\{\chi \in C^0(\overline{\Omega}) \colon \chi|_\tau \in P_m, \; \tau \in \mathcal{T}^h\right\} \;, \tag{4.3}$$

where P_m denotes the set of polynomials of degree less than or equal to m. The following continuous in time Galerkin approximation was first proposed by Elliott, French and Milner [19]: find $\{u^h(x,t), w^h(x,t)\}$: $[0,T] \to S^h \times S^h$ such that

$$\left(\frac{\partial u^h}{\partial t}, \chi\right) + (\nabla w^h, \nabla \chi) = 0\,, \quad \forall \chi \in S^h \tag{4.4a}$$

$$\gamma(\nabla u^h, \nabla \chi) + (\phi(u^h) + f, \chi) = (w^h, \chi)\,, \quad \forall \chi \in S^h \tag{4.4b}$$

$$u^h(x,0) = u_0^h(x)\,, \tag{4.4c}$$

where $u_0^h \in S^h$ is a suitable approximation to u_0.

In the case $f = 0$, Elliott, French and Milner [19] proved global existence of solutions to (4.4) and in the practical case of peicewise linear elements together with numerical integration they obtained various optimal order error bounds. It is the purpose of this section to extend their analysis to fully discrete schemes based upon time discretising (4.4). We consider the following schemes:

(S1) Find for each $n \geq 1$ $\{U^n, W^n\} \in S^h \times S^h$ such that for $n \geq 0$

$$(\partial_t U^n, \chi)^h + (\nabla W^{n+1}, \nabla \chi) = 0\,, \quad \forall \chi \in S^h \tag{4.5a}$$

$$(W^{n+1}, \chi)^h = \gamma(\nabla U^{n+1}, \nabla \chi) + (\phi(U^{n+1}), \chi)^h + (f, \chi)^h, \quad \forall \chi \in S^h \tag{4.5b}$$

and

$$U^0 = u_0^h\,. \tag{4.5c}$$

(S2) Find for each $n \geq 1$ $\{U^n, W^n\} \in S^h \times S^h$ such that for $n \geq 0$

$$(\partial_t U^n, \chi)^h + (\nabla W^{n+1}, \nabla \chi) = 0\,, \quad \forall \chi \in S^h \tag{4.6a}$$

$$(W^{n+1}, \chi)^h = \gamma(\nabla U^{n+1/2}, \nabla \chi) + (\hat{\phi}(U^n, U^{n+1}), \chi)^h + (f, \chi)^h, \quad \forall \chi \in S^h \tag{4.6b}$$

and

$$U^0 = u_0^h\,. \tag{4.6c}$$

Here we have used the notation

$$\partial_t V^n = \frac{V^{n+1} - V^n}{\Delta t}, \qquad V^{n+1/2} = \frac{1}{2}\left(V^{n+1} + V^n\right),$$

where Δt is the time step and

$$\hat{\phi}(r,s) \equiv \begin{cases} \dfrac{\psi(r) - \psi(s)}{r - s}, & r \neq s \\ \psi'(r), & r = s. \end{cases} \tag{4.7}$$

Clearly $\hat{\phi}(r,s)$ is a second order approximation in $|r-s|$ to $\phi(\frac{r+s}{2})$ and thus we expect that (4.6) is a second order in Δt perturbation of the Crank-Nicolson scheme (S3) which is (S2) with (4.6b) replaced by

(4.8)

$$(W^{n+1},\chi)^h = \gamma(\nabla U^{n+1/2},\nabla\chi) + (\phi(U^{n+1/2}),\chi)^h + (f,\chi)^h, \quad \forall \chi \in S^h.$$

Furthermore we have used the notation $(\cdot,\cdot)^h$ for an inner product on S^h (and $C(\Omega)$) which is either the $L^2(\Omega)$ inner product or an approximation to the $L^2(\Omega)$ inner product using appropriate numerical quadrature based on nodal values. (e.g. mass lumping for linear triangular elements) It is convenient for our purpose here to assume that $|\cdot|_h = ((\cdot,\cdot)^h)^{1/2}$ is a norm on S^h and that

$$(\chi, v)^h = (\chi\, v, 1)^h, \quad \forall \chi, v \in S^h, \tag{4.9a}$$

$$|\chi|_h \leq C\Big(|\chi|_1 + |(\chi,1)^h|\Big). \tag{4.9b}$$

The scheme (S2) was proposed by Qiang Du and Nicolaides [47] for the one dimensional Cahn-Hilliard equation with Dirichlet boundary conditions. They obtained optimal error bounds for computations on a finite time interval provided that $\Delta t \leq C h^2$. The latter condition was needed for existence and uniqueness of the discrete solution. In the following we shall show that schemes (S1) and (S2) are well defined for $\Delta t \leq \Delta t^*$ where Δt^* depends only on the partial differential equation and not on h. Furthermore we consider the asymptotic behaviour of $\{U^n, W^n\}$ as $n \to \infty$.

A standard conforming finite element Galerkin method for the fourth order equation

$$u_t = -\gamma\,\Delta^2 u + \Delta\phi(u)\ ,$$

requires that the approximating space be in $H^2(\Omega)$. In one space dimension error bounds were obtained by Elliott and Zheng [21] and numerical computations were performed by Elliott and French [17]. Another possibility is the use of non-conforming finite elements; see Elliott and French [18] for a two dimensional analysis. See also French and Nicolaides [22] for a finite difference scheme.

Proposition 4.1. *The sequences $\{U^n, W^n\}$ generated by (S1) and (S2) satisfy:*

(4.10a) $$(U^n, 1)^h = (u_0^h, 1)^h$$

(4.10b) (S1) $$\forall\epsilon > 0,\ \ \mathcal{E}^h(U^{n+1}) - \mathcal{E}^h(U^n) + \Delta t\,(1-\epsilon)\,|W^{n+1}|_1^2 + \\ + \frac{1}{2}\Big(\gamma - \frac{\Delta t\,\beta^4}{8\,\epsilon}\Big)\,|U^{n+1} - U^n|_1^2 \le 0\ ,$$

(4.10c) (S2) $$\mathcal{E}^h(U^{n+1}) - \mathcal{E}^h(U^n) + \Delta t\,|W^{n+1}|_1^2 = 0\ ,$$

where

(4.11) $$\mathcal{E}^h(\chi) = \frac{\gamma}{2}\,|\chi|_1^2 + (\psi(\chi), 1)^h + (f, \chi)^h\ .$$

Proof: The conservation equation (4.10a) is an immediate consequence of taking $\chi = 1$ in (4.5a) and (4.6a). Let us first consider (S1). Taking $\chi = W^{n+1}$ in (4.5a), and $\chi = (U^{n+1} - U^n)$ in (4.5a 4.5b) yields

(4.12a) $$(U^{n+1} - U^n, W^{n+1})^h + \Delta t\,|W^{n+1}|_1^2 = 0$$

(4.12b) $$(W^{n+1}, U^{n+1} - U^n)^h - \gamma\Big(\nabla U^{n+1}, \nabla(U^{n+1} - U^n)\Big) = \\ = \Big(\phi(U^{n+1}), U^{n+1} - U^n\Big)^h + (f, U^{n+1} - U^n)^h$$

(4.12c) $$|U^{n+1} - U^n|_h^2 = -\Delta t\,\Big(\nabla W^{n+1}, \nabla(U^{n+1} - U^n)\Big)\ .$$

Recalling the condition $\psi''(r) \geq -\beta^2$, $\forall\, r \in \mathbf{R}$, it follows from a Taylor expansion that

$$(4.13)\quad \psi(s) - \psi(r) + \psi'(r)\,(r-s) = -\frac{\psi''(z)}{2}\,(r-s)^2 \leq \frac{\beta^2}{2}\,(r-s)^2 .$$

Combining (4.12a) and (4.12b) we obtain

$$\begin{aligned}(4.14)\quad & \mathcal{E}^h(U^{n+1}) - \mathcal{E}^h(U^n) + \Delta t\,|W^{n+1}|_1^2 + \frac{\gamma}{2}\,|U^{n+1} - U^n|_1^2 = \\ &= \left(\psi(U^{n+1}) - \psi(U^n), 1\right)^h + \left(\phi(U^{n+1}), U^n - U^{n+1}\right)^h \\ &\leq \frac{\beta^2}{2}\,|U^{n+1} - U^n|_h^2 = -\frac{\Delta t\,\beta^2}{2}\,(\nabla W^{n+1}, \nabla U^{n+1} - \nabla U^n)\,,\end{aligned}$$

where we have used the properties of $(\cdot,\cdot)^h$, (4.13) and (4.12c). Inequality (4.10b) is an immediate consequence of (4.14). In the case of (S2) a similar but simpler argument is used. Taking $\chi = W^{n+1}$ in (4.6a) and $\chi = U^{n+1} - U^n$ in (4.6b) yields

$$(4.15\text{a})\qquad (U^{n+1} - U^n, W^{n+1})^h + |W^{n+1}|_1^2 = 0$$

$$\begin{aligned}(4.15\text{b})\qquad & (U^{n+1} - U^n, W^{n+1})^h - \frac{\gamma}{2}\,|U^{n+1}|_1^2 + \frac{\gamma}{2}\,|U^n|_1^2 = \\ &= \left(\hat{\phi}(U^n, U^{n+1}), U^{n+1} - U^n\right)^h + (f, U^{n+1} - U^n)^h .\end{aligned}$$

By definition

$$(4.16)\qquad \left(\hat{\phi}(U^n, U^{n+1}), U^{n+1} - U^n\right)^h = \left(\psi(U^{n+1}) - \psi(U^n), 1\right)^h$$

and (4.10c) follows by combining (4.15a) (4.15b). ∎

We now prove that there exist sequences $\{U^n, W^n\}$ satisfying (S1) and (S2) and that these sequences are unique for Δt sufficiently small but independent of h.

It is convenient to introduce a discrete Green's operator approximating the inverse of the Laplacian with Neumann boundary conditions defined by:

$$(4.17\text{a})\qquad \mathcal{G}_{\mathrm{N}}^h \in \mathcal{L}(S_0^h, S_0^h)\,, \qquad S_0^h = \{\chi \in S^h \colon (1,\chi)^h = 0\}$$

$$(4.17\text{b})\qquad (\nabla \mathcal{G}_{\mathrm{N}}^h v, \nabla \chi) = (v,\chi)^h\,, \qquad \forall \chi \in S^h$$

and which satisfies

$$|\chi|_{-h}^2 \equiv |\mathcal{G}^h \chi|_1^2 = (\mathcal{G}^h\chi,\chi)^h = (\chi,\mathcal{G}^h\chi)^h . \tag{4.18}$$

The existence and uniqueness of $\mathcal{G}_N^h v$ solving (4.17b) follows from the discrete Poincaré inequality (4.9b)

Theorem 4.1. *There exists $\{U^n, W^n\}$ satisfying (S1) and (S2). Furthermore if $\Delta t \leq \Delta t^*$*

$$\text{for (S1)} \quad \Delta t^* = \frac{4\gamma}{\beta^4} \tag{4.19a}$$

and

$$\text{for (S2)} \quad \Delta t^* = \frac{8\gamma}{\beta^4} \tag{4.19b}$$

then the sequences are uniquely defined.

Proof: We first prove the results for the scheme (S1). Consider the variational problem

$$\text{(V.P.)} \quad \min_{\chi\in K^h} J^h(\chi) = J^h(U) , \tag{4.20a}$$

where

$$K^h = \{\chi \in S^h : (\chi - U^n, 1)^h = 0\} \tag{4.20b}$$

and

$$J^h(\chi) = \mathcal{E}^h(\chi) + \frac{1}{2\,\Delta t}|\chi - U^n|_{-h}^2 . \tag{4.20c}$$

Since $J^h(\cdot)$ is continuous and, using the non-negativity of $\psi(\cdot)$,

$$J^h(\chi) \geq \frac{\gamma}{2}|\chi|_1^2 + (f,\chi)^h \geq \frac{\gamma}{4}|\chi|_1^2 - C(f) , \quad \forall \chi \in S^h ,$$

it follows that there exists a solution to (V.P.). Such a minimiser is a critical point of $J^h(\cdot)$ satisfying,

$$0 = \gamma(\nabla U, \nabla\chi) + (\phi(U),\chi)^h + (f,\chi)^h + \Big(\mathcal{G}^h\Big(\frac{U-U^n}{\Delta t}\Big),\chi\Big)^h - \lambda(1,\chi)^h ,$$

where λ is the Lagrange multiplier for the constraint (4.20b). By comparison with (4.5a), (4.5b) and (4.17) setting

$$U^{n+1} = U\,, \qquad W^{n+1} = \lambda - \mathcal{G}^h\Big(\frac{U - U^n}{\Delta t}\Big)\,,$$

we find that $\{U^{n+1}, W^{n+1}\}$ solve (4.5a) and (4.5b).

In order to prove uniqueness, set θ^U and θ^W to be the differences of two possible solutions $\{U^{n+1}, W^{n+1}\}$. By subtraction it follows that

$$(4.21a) \qquad (\theta^U, \chi)^h + \Delta t\,(\nabla\theta^W, \nabla\chi) = 0\,, \qquad \forall\,\chi \in S^h$$

$$(4.21b) \qquad (\theta^W, \chi)^h - \gamma(\nabla\theta^U, \nabla\chi) = \big(\phi(U_1^{n+1}) - \phi(U_2^{n+1}), \chi\big)^h\,.$$

Taking $\chi = \theta^W$ in (4.21a) and $\chi = \theta^U$ in (4.21b) and using the mean value theorem to obtain

$$(r - s)\,(\phi(r) - \phi(s)) = \psi''(z)(r - s)^2 \geq -\beta^2\,(r - s)^2\,,$$

we have that

$$\begin{aligned}\gamma\,|\theta^U|_1^2 + \Delta t\,|\theta^W|_1^2 &\leq \beta^2(\theta^U, \theta^U)^h = -\Delta t\,\beta^2(\nabla\theta^U, \nabla\theta^W)\\ &\leq \Delta t\,\beta^2\,|\theta^U|_1\,|\theta^W|_1 \leq \frac{\Delta t}{4}\,\beta^4\,|\theta^U|_1^2 + \Delta t\,|\theta^W|_1^2\,.\end{aligned}$$

Uniqueness is an immediate consequence of the above inequality and the observations that $(\theta^U, 1)^h = 0$ and that the discrete Poincaré inequality (4.9b) holds.

We turn to scheme (S2). Choosing Ψ^n so that

$$(4.22a) \qquad (\Psi^n)'(\chi)(x) \equiv \hat{\phi}(\chi, U^n)(x)\,, \qquad \Psi^n(\chi)(x) \geq 0\,,$$

and setting

$$\begin{aligned}(4.22b) \qquad J_n^h(\chi) = \frac{\gamma}{4}\,|\chi|_1^2 + (\Psi^n(\chi), 1)^h + \frac{1}{2\,\Delta t}\,|\chi - U^n|_{-h}^2\\ + \frac{\gamma\,\Delta t}{2}\,(\nabla U^n, \nabla\chi) + (f, \chi)^h\,,\end{aligned}$$

we may use the same argument as above to show the existence of $\{U^{n+1}, W^{n+1}\}$ satisfying (4.6a) and (4.6b).

In order to prove uniqueness, set θ^U and θ^W to be the differences of two possible solution $\{U_i^{n+1}, W_i^{n+1}\}$ for $(i = 1,2)$. By subtraction it follows that

$$(4.23a)\quad (\theta^U, \chi)^h + \Delta t\,(\nabla\theta^W, \nabla\chi) = 0\,, \qquad \forall\chi \in S^h\,,$$

$$(4.23b)\quad (\theta^W, \chi)^h = \frac{\gamma}{2}(\nabla\theta^U, \nabla\chi) + \left(\hat\phi(U^n, U_1^{n+1}) - \hat\phi(U^n, U_2^{n+1}), \chi\right)^h.$$

Observe that (using standard finite difference notation)

$$\begin{aligned}\left(\hat\phi(r,s_1) - \hat\phi(r,s_2)\right)(s_1 - s_2) = \\ &= \frac{1}{s_1 - s_2}\left(\frac{\psi(s_1) - \psi(r)}{s_1 - r} - \frac{\psi(s_2) - \psi(r)}{s_2 - r}\right)(s_1 - s_2)^2 \\ &= \psi\,[s_1, r, s_2]\,(s_1 - s_2)^2 \\ &= \frac{\psi''(z)}{2}(s_1 - s_2)^2\,,\end{aligned}$$

where z lies in the smallest interval containing s_1, r and s_2. Since $\psi''(z) \geq -\beta^2$, $\forall z \in \mathbf{R}$, it follows that

$$(4.24)\qquad \left(\hat\phi(r,s_1) - \hat\phi(r,s_2)\right)(s_1 - s_2) \geq -\frac{\beta^2}{2}(s_1 - s_2)^2\,.$$

By consideration of (4.23) and (4.24) we obtain condition (4.19b) for uniqueness of solutions to (S2) using an identical argument to that employed earlier for the scheme (S1). ∎

Numerical schemes for solving a nonlinear evolution equation over a long time interval should simulate the asymptotic behaviour of the underlying equation. Schemes (S1) and (S2) possess a similar asymptotic behaviour as that described in section 3. Let C_h be the set of critical points of $\mathcal{E}^h(\chi) = \frac{\gamma}{2}|\chi|_1^2 + (\psi(\chi), 1)^h + (f, \chi)^h$ over the set $K^h = \{\chi \in S^h\colon (\chi, 1)^h = (u_0^h, 1)^h\}$.

Thus $U^* \in C_h$ if $U^* \in K^h$ and

$$(4.25)\qquad \gamma(\nabla U^*, \nabla\chi) + (\phi(U^*), \chi)^h = (W^*, \chi)^h\,, \qquad \forall\chi \in S^h\,,$$

where $W^* \in \mathbf{R}$.

Theorem 4.2. *Let $\Delta t \leq \frac{1}{2}\Delta t^*$ and $\{U^n, W^n\}$ be the uniquely defined sequences from either (S1) or (S2). Then there exists a sequence $\{U^{n_p}, W^{n_p}\}$ which converges to $\{U^*, W^*\} \in C_h \times \mathbf{R}$ solving (4.25). Furthermore if C_h consists of isolated points then the whole sequence converges to the same limit $\{U^*, W^*\} \in C_h \times \mathbf{R}$.*

Proof: The proof depends upon the estimate of Proposition 4.1 which shows that $\mathcal{E}^h(\cdot)$ is a Lyapunov functional for schemes (S1) and (S2). We deal only with (S2) as the proof for (S1) is similar. Implicit use will be made of the fact that S^h is finite dimensional so that the bounded sets are compact and norms are equivalent. Summing (4.10c) over n yields

$$\mathcal{E}^h(U^n) + \Delta t \sum_{j=1}^{n} |W^j|_1^2 = \mathcal{E}^h(u_0^h)$$

and since

$$\mathcal{E}^h(U^n) \geq \frac{\gamma}{4}|U^n|_1^2 - C(f) ,$$

it follows that

$$|U^n|_1^2 + \Delta t \sum_{j=1}^{n} |W^j|_1^2 \leq C, \quad \forall n . \tag{4.26}$$

Noting that $U^n \in K^h$ and the discrete Poincaré inequality (4.9b), it holds that $(|U^n|_0 + |U^n|_1)$ is uniformly bounded. Hence there exists a subsequence $\{U^{n_p}\}$ converging to a $U^* \in K^h$. Furthermore it follows from (4.26) that $\lim_{n\to\infty} |W^n|_1 = 0$ and thus from (4.6a) that $\lim_{n\to\infty} |U^n - U^{n+1}|_h = 0$. Therefore $\lim_{n_p\to\infty} U^{n_p+1} = U^*$ and since $\hat{\phi}(\cdot,\cdot)$ is continuous it follows that

$$\lim_{n_p\to\infty} \hat{\phi}(U^{n_p}, U^{n_p+1}) = \phi(U^*) .$$

Taking $\chi = 1$ in (4.6b) and passing to the limit implies

$$\lim_{n_p\to\infty} (W^{n_p}, 1) = (\phi(U^*), 1)^h + (f, 1)^h \equiv (W^*, 1)^h, \quad W^* \in \mathbf{R} ;$$

$$\text{hence } \lim_{n_p\to\infty} W^{n_p} = W^* .$$

We can now pass to the limit in (4.6b) and obtain (4.25).

In order to prove the last statement we require the inequality, the proof of which we postpone,

$$(4.27)\qquad \|U^* - U^{n+1}\| \le \mu \|U^* - U^n\|, \quad \forall n ,$$

for some $\|\cdot\|$, where $\mu > 1$ is independent of n but may depend on Δt and h and $U^* \in C_h$ is any limit point of $\{U^n\}$. Set

$$B(U^*,\epsilon) \equiv \left\{\chi \in S^h \colon \|\chi - U^*\| < \epsilon\right\}$$

and let U^* be the only element of C_h in $B(U^*, 2\,\delta)$. Let $\{U^{n_p}\}$ be a subsequence of $\{U^n\}$ such that $\{U^{n_p}\} \in B(U^*, \delta/\mu)$. It follows from (4.27) that

$$\{U^{n_p+1}\} \in B(U^*, \delta) .$$

Thus either there exists an infinite subsequence $\{U^{n_k}\} \in B(U^*, \delta)\backslash B(U^*, \delta/\mu)$ or not. If not then this implies that the whole sequence converges to U^*. If there exists such an infinite subsequence then there is a limit in $\overline{B}(U^*, \delta)\backslash B(U^*, \delta/\mu)$ which contradicts the uniqueness of U^* in $B(U^*, 2\delta)$.

We now turn to the proof of (4.27).

Set $\theta_n^W = W^* - W^n$ and $\theta_n^U = U^* - U^n$. It follows that from (4.6) and (4.25) using similar arguments to those employed in the proof of uniqueness that

$$(4.28a)\qquad \Delta t\, |\theta_{n+1}^W|_1^2 + \frac{\gamma}{2}\, |\theta_{n+1}^U|_1^2 =$$

$$= (\theta_n^U, \theta_{n+1}^W)^h - \frac{\gamma}{2}\, (\nabla\theta_n^U, \theta_{n+1}^U) - \left(\phi(U^*) - \hat{\phi}(U^n, U^{n+1}), U^* - U^{n+1}\right)^h$$

and

$$(4.28b)\qquad |\theta_{n+1}^U|_h^2 \le |\theta_n^U|_h\, |\theta_{n+1}^U|_h + \Delta t\, |\theta_{n+1}^W|_1\, |\theta_{n+1}^U|_1 \,.$$

Since S^h is finite dimensional the estimate (4.10c) implies that $\|U^n\|_{L^\infty} \le C$, $\forall n$ where C may depend on h and Δt. Thus a calculation reveals that

$$(4.29a)\qquad |\phi(U^*) - \hat{\phi}(U^n, U^{n+1})| \le C\, (|\theta_n^U| + |\theta_{n+1}^U|)$$

$$(4.29b)\quad -\left(\phi(U^*) - \hat{\phi}(U^n,U^{n+1}), \theta_{n+1}^U\right)^h \le C\, |\theta_n^U|_h\, |\theta_{n+1}^U|_h + \frac{\beta^2}{2}\, |\theta_{n+1}^U|_h^2 .$$

Since

$$(\theta^W_{n+1}, 1)^h = \left(\phi(U^*) - \hat{\phi}(U^n, U^{n+1}), 1\right)^h$$

and noting the Poincaré inequality (4.9b) we may combine (4.28) and (4.29) in order to obtain (4.27).

5 – Numerical Simulations

There have been numerous computational studies of the Cahn--Hilliard model for phase separation in one and two dimension. These numerical experiments display many features of spinodal decomposition found by experimental studies of alloys and tend to support the view that the Cahn-Hilliard theory qualitatively models spinodal decomposition.

Numerical experiments in one space dimension with initial compositions being perturbations of a uniform state in the spinodal interval $[u^s_a, u^s_b]$ show that the concentration rapidly evolves into a 'fine' grained structure with interfaces separating 'grains' defined by the uniform values u_a and u_b, i.e. phase separation. The scale of these patterns in the very early stages is in line with the linear theory of Section 3.1 See Elliott and French [17] and Copetti [in preparation]. After this rapid evolution into a phase separated structure, the coarse grains grow and shrink as interfaces migrate and disappear. This coarsening process takes place on a longer time scale; indeed the larger the grains the slower the coarsening process. It is very easy in numerical computations to mistake a slowly evolving non-stationary pattern for a steady state.

Numerical experiments in two dimensions also display these two features of rapid phase separation followed by a slower coarsening process. Furthermore the morphology of the interfaces is more interesting; the typical pattern for spinodal decomposition is a highly inter-connected fat spaghetti like structure which contrasts with the separated growing blobs associated with nucleation and growth. In Figures 3 a,b,c,d,e,f,g and 4 a,b,c,d,e we show two dimensional patterns for spinodal decomposition obtained by Copetti [in preparation]. A finite difference simulation was performed on the Cahn-

-Hilliard equation with periodic boundary conditions, $\gamma = \frac{1}{2}$, $\phi(u) = \frac{1}{2}(u^3 - u)$ and the initial condition being a random perturbation of the state $u = 0$.

In Figure 3 the black dots denote phase **B**. In figure 4 the concentration is plotted against (x_1, x_2).

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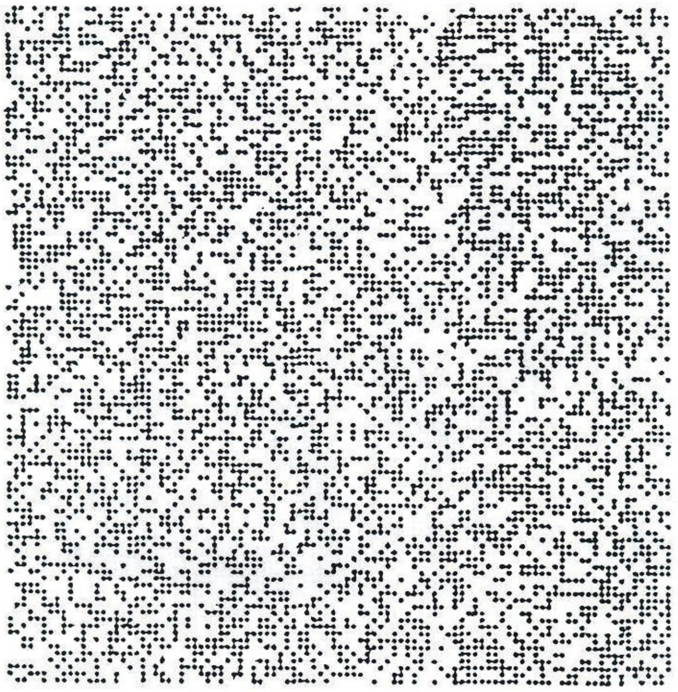

Fig. 3a: $t = 0$.

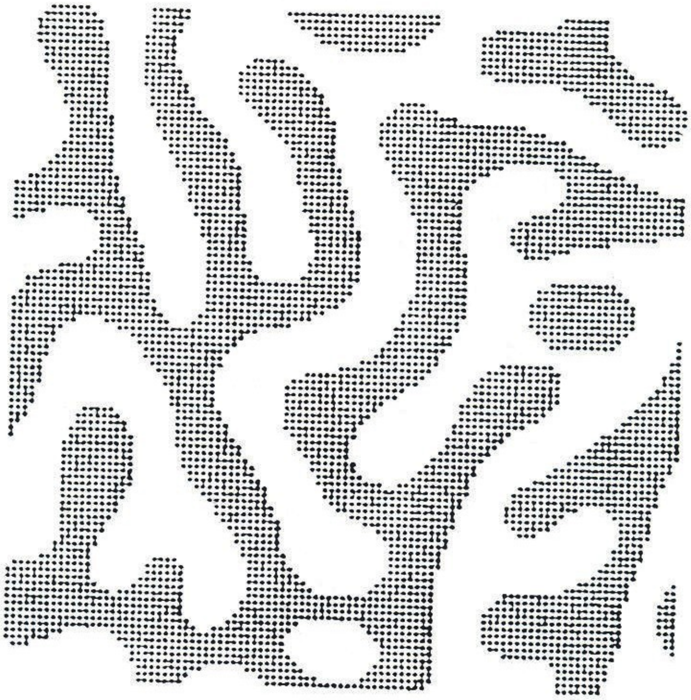

Fig. 3b: $t = 2\,400$.

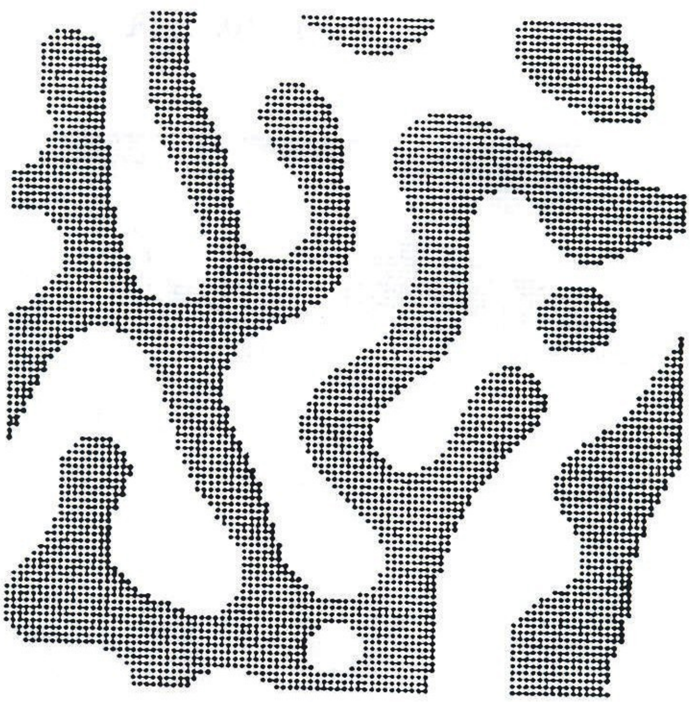

Fig. 3c: $t = 4\,800$.

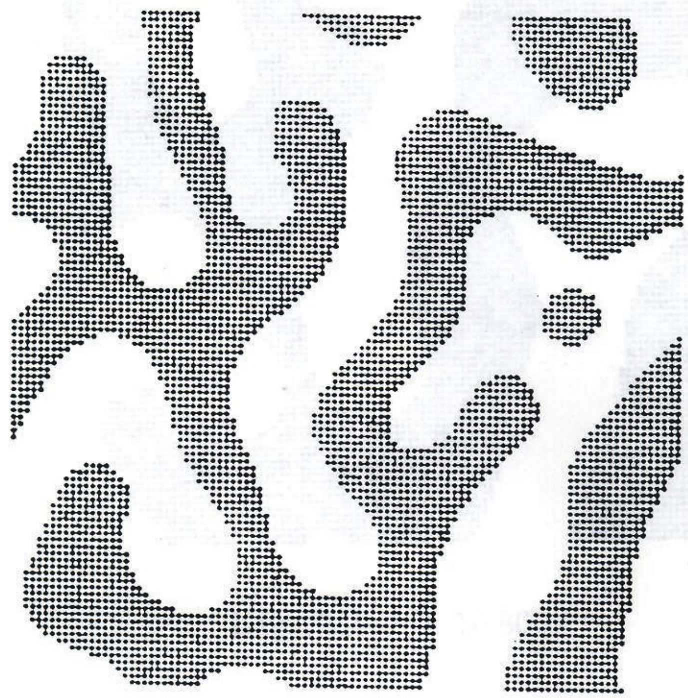

Fig. 3d: $t = 7\,200$.

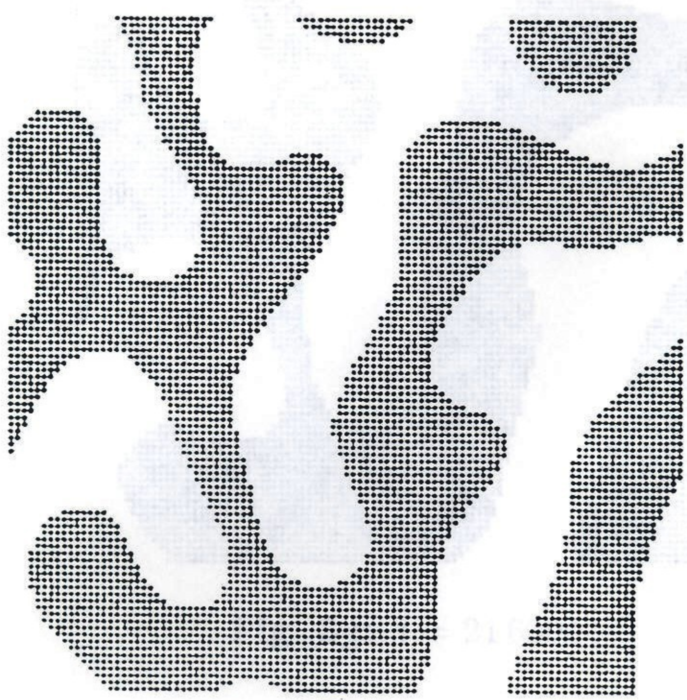

Fig. 3e: $t = 12\,000$.

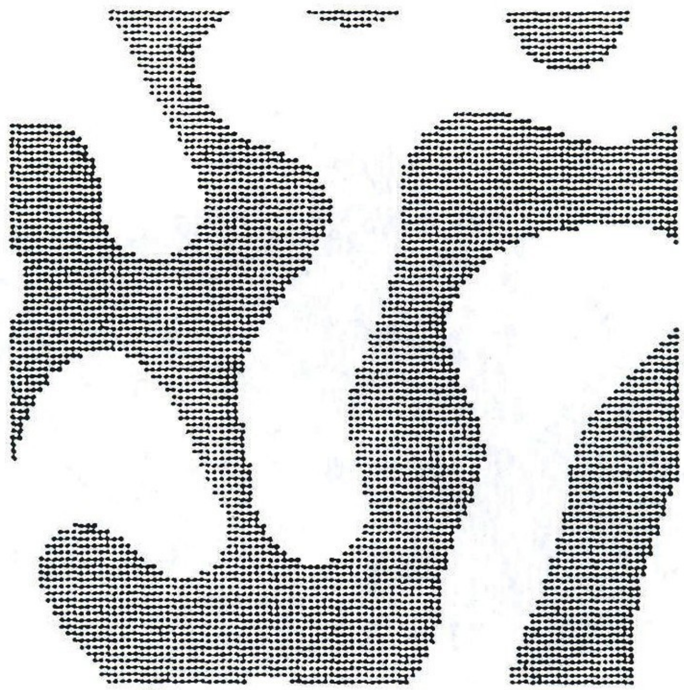

Fig. 3f: $t = 16\,800$.

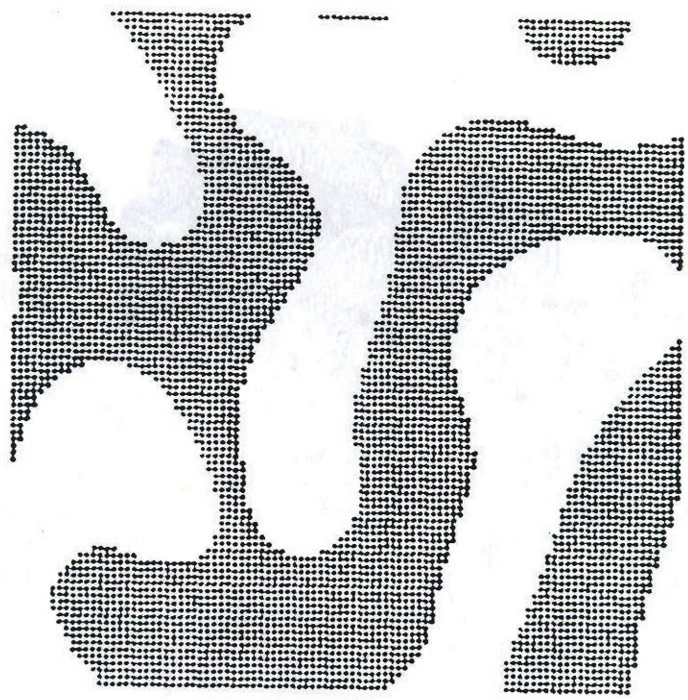

Fig. 3g: $t = 21\,600$.

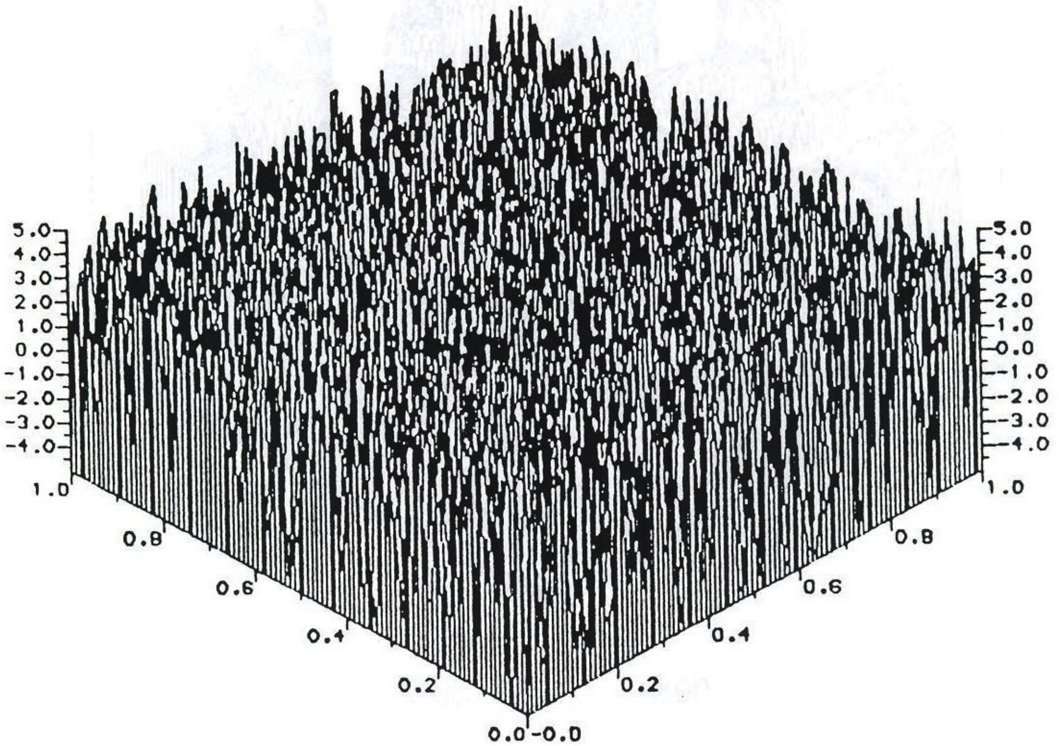

Fig. 4a: $t = 0$.

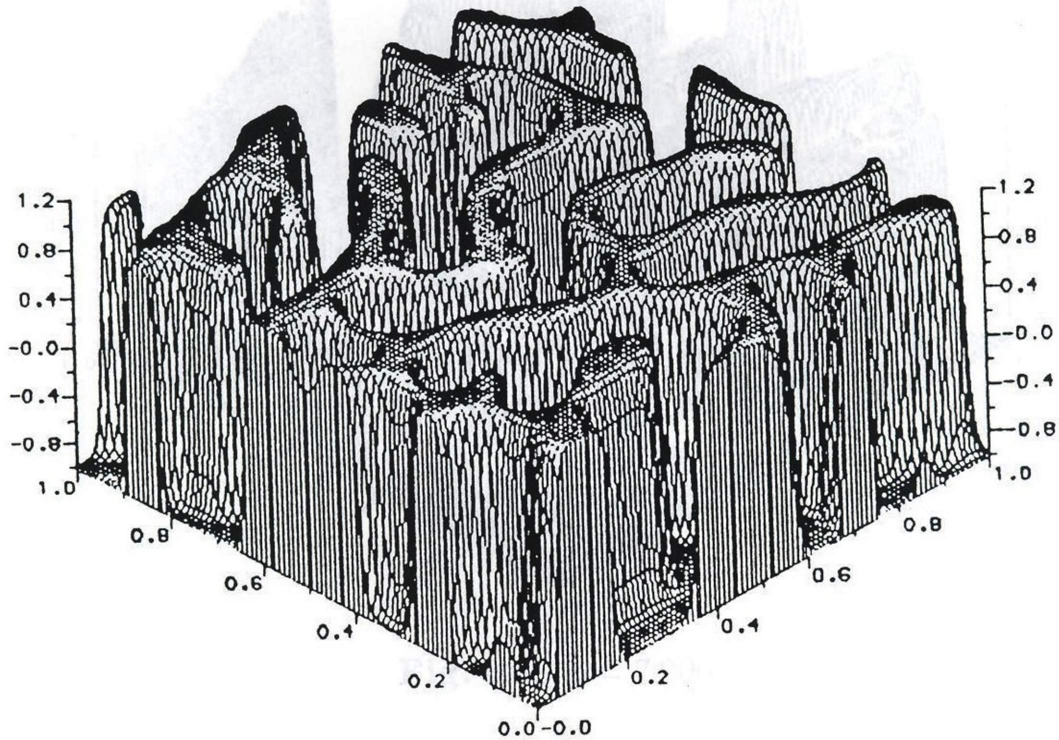

Fig. 4b: $t = 2\,400$.

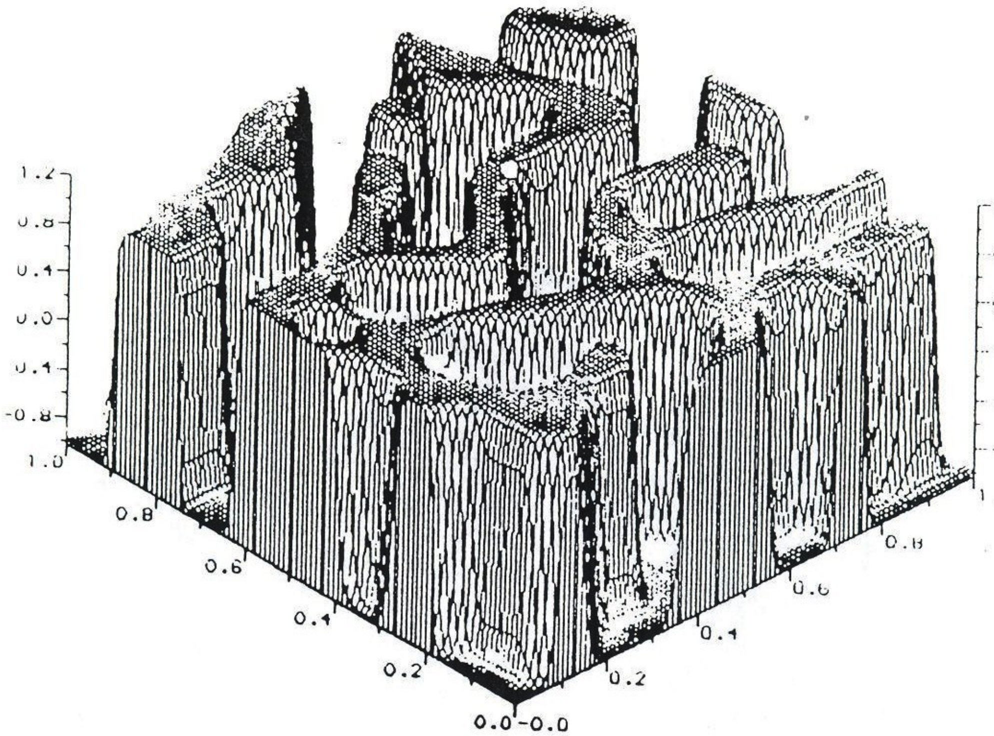

Fig. 4c: $t = 4\,800$.

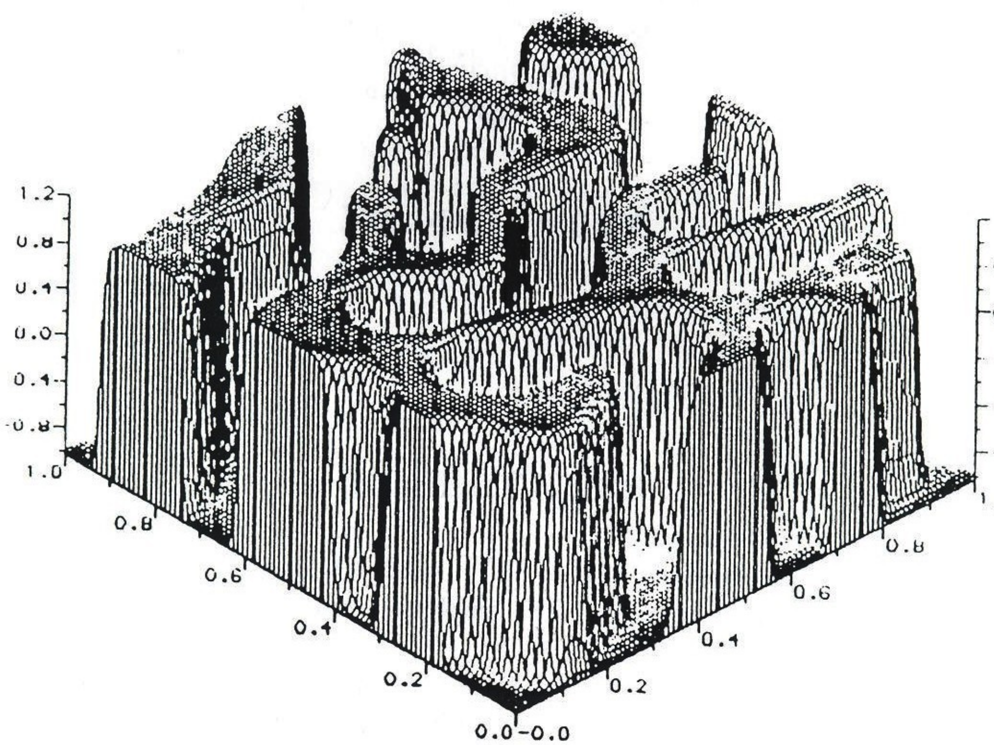

Fig. 4d: $t = 7\,200$.

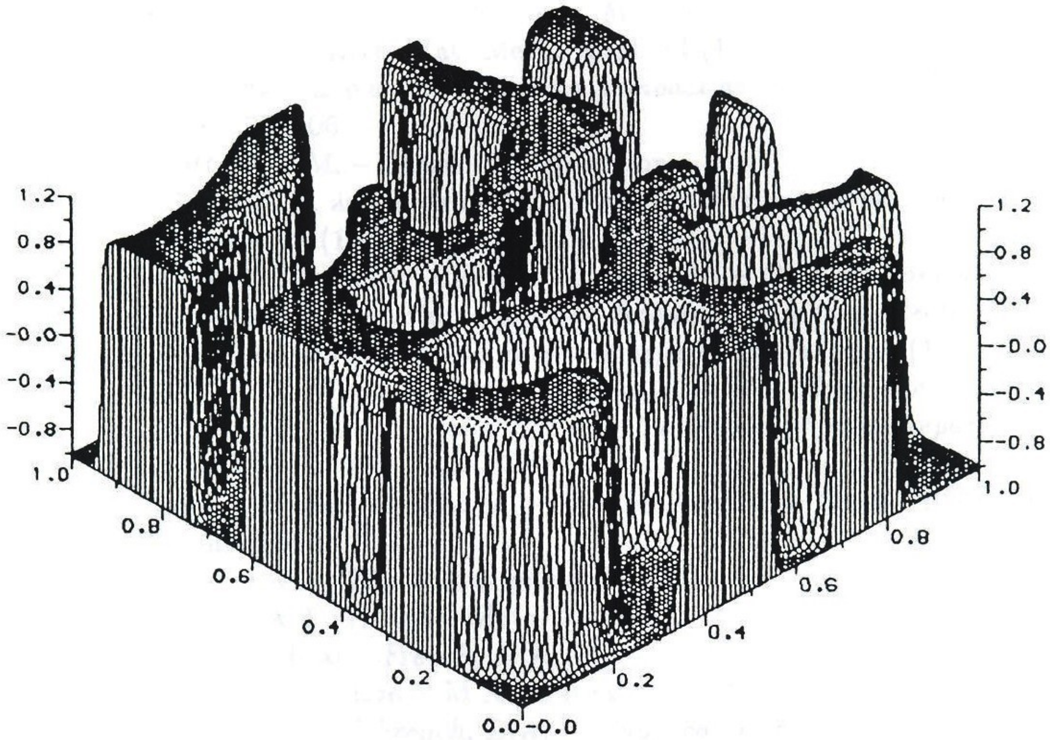

Fig. 4e: $t = 9600$.

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