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Front migration in the nonlinear Cahn–Hilliard equation

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The method of matched asymptotic expansions is used to describe solutions of the nonlinear Cahn–Hilliard equation for phase separation in $N > 1$ space dimensions. The expansion is formally valid when the thickness of internal transition layers is small compared with the distance separating layers and with their radii of curvature. On the dominant (slowest) timescale the interface velocity is determined by the mean curvature of the interface, by a non-local relation which is identical to that in a well-known quasi-static model of solidification, which exhibits a shape instability discovered by Mullins & Sekerka (*J. appl. Phys.* **34**, 323–329 (1963)). On a faster timescale, the Cahn–Hilliard equation regularizes a classic two-phase Stefan problem. Similarity solutions of the two-phase Stefan problem should describe boundary layers. Existence and uniqueness of such similarity solutions which admit metastable states is proved rigorously in an appendix.

1. INTRODUCTION

In the process of spinodal decomposition, a miscible chemical mixture is quenched into an unstable state and proceeds to separate into distinct phases by diffusion against concentration gradients. One model for this process is the nonlinear Cahn–Hilliard equation (cf. Cahn 1961); let $u(x, t)$ be the concentration of one species of the mixture, for x in a domain Ω in \mathbb{R}^N . Starting with a free energy functional of the form

$$I(u) = \int_{\Omega} F(u(x)) + \frac{1}{2}\epsilon^2 |\nabla u(x)|^2 dx, \quad (1.1)$$

where F is a (non-convex) bulk free energy density as implied by figure 1, take the chemical potential in the form

$$\mu = \delta I / \delta u = F'(u) - \epsilon^2 \Delta u. \quad (1.2)$$

Then from the diffusion equation, $u_t = \Delta \mu$, one obtains the Cahn–Hilliard equation,

$$u_t = \Delta(F'(u) - \epsilon^2 \Delta u). \quad (1.3)$$

I have taken the simplest form here, neglecting concentration dependence of the mobility and gradient–energy coefficients. Boundary conditions may be taken to be of Neumann type,

$$\left. \begin{aligned} \mathbf{n} \cdot \nabla \mu &= 0 \quad (\text{no flux}), \\ \mathbf{n} \cdot \nabla u &= 0 \quad (\text{variational}), \end{aligned} \right\} \quad (1.4)$$

where \mathbf{n} is the outward unit normal to $\partial\Omega$, or of Dirichlet type,

$$\left. \begin{aligned} \mu &= \mu_b \quad (\text{fixed potential}), \\ u &= u_b \quad (\text{variational}). \end{aligned} \right\} \quad (1.5)$$

For each type of boundary condition, the variational condition guarantees that the first variation $\delta I/\delta u$ contains no boundary terms, so (1.2) holds. Phases of the mixture corresponds to intervals of monotonicity of $F'(u)$. A state u is called stable, metastable or unstable according to whether it corresponds to a homogeneous state which is a global minimizer, local but not global minimizer, or local non-minimizer respectively, for the free energy functional in (1.1) when $\epsilon = 0$, at constant average concentrations. For $F'(u)$ as in figure 1, states u satisfying $u \leq u_-^m$ or $u \geq u_+^m$ are stable, states satisfying $u_-^m < u < u_-^s$ or $u_+^s < u < u_+^m$ are metastable, and states satisfying $u_-^s \leq u \leq u_+^s$ are unstable.

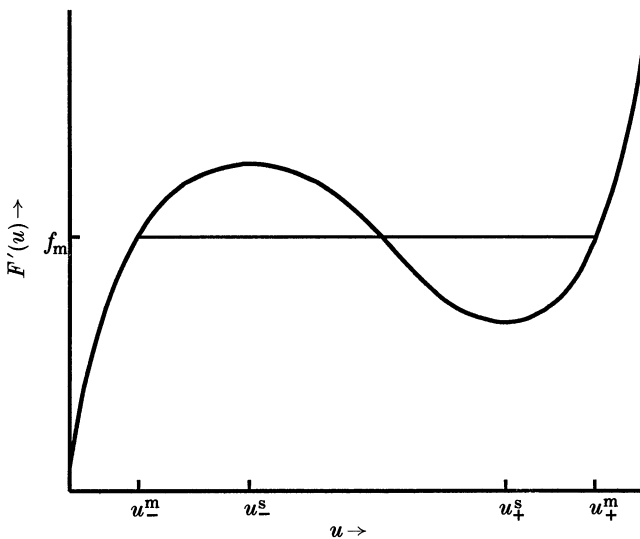


FIGURE 1. Bulk chemical potential.

Experimental investigation of the validity of the Cahn–Hilliard equation has been largely limited to the early-time linear régime, where long-wavelength and perturbations of a homogeneous unstable state grow exponentially and equation (1.3) may be solved analytically. Recent surveys are given by Skripov & Skripov (1979), Gunton & Droz (1983), Lipatov & Shilov (1984) and Nose (1987). The linear Cahn–Hilliard equation has been quantitatively validated only rarely, however, for various reasons, including the short time of validity of the linear régime, too-large initial fluctuations, and other relevant dynamic effects such as thermal noise, coherency strain and coupling to other slow variables. But some have expressed the belief (see, for example, Binder 1981) that the nonlinear Cahn–Hilliard equation, with noise, should correctly describe the whole process of phase separation by spinodal decomposition.

Recent numerical experiments and minimization studies have supported this

belief. In the numerical experiments of Elliot & French (1987) in one dimension, a solution, initially a perturbation of an unstable state in the spinodal interval $[u_-^s, u_+^s]$ in figure 1, quickly develops a pattern of interfaces separating domains at approximate phase equilibrium, with the scale as suggested by linear theory. A nonlinear coarsening process ensues on a much slower timescale, as interfaces migrate and annihilate each other. Pattern development was found early on by deFontaine (cf. Hilliard 1970), and the very interesting coarsening process has recently been studied numerically in two dimensions by Rogers *et al.* (1988), and even in three dimensions by Gawlinski *et al.* (1989). These authors observe self-similar scaling of the structure function not dissimilar to that seen in experiments and Ising model simulations. Since $dI(u)/dt \leq 0$, the system should progress toward a stable equilibrium state, a global minimizer of $I(u)$. Such minimizers have been rigorously characterized in the limit $\epsilon \rightarrow 0$ as mixtures which minimize the area of the interface between the phases (cf. Carr *et al.* 1984; Sternberg 1988; Modica 1987).

In this paper I seek to give a systematic formal asymptotic description of the solution of the Cahn–Hilliard equation in a régime corresponding to the later stages of phase separation, when interfacial thickness, which is proportional to ϵ , is small compared with the radii of curvature and separation of interfaces. But the geometric arrangement of interfaces is allowed to be arbitrary, not restricted to combinations of spheres, say, so that one may consider complicated geometries such as may arise from spinodal decomposition (cf. Skripov & Skripov 1979; Rogers *et al.* 1988). The solution will be described on successive timescales, starting with initial data of the following type; I suppose that at time $t = 0$, a smooth front Γ_0 is specified, independent of ϵ . Arbitrary, smooth, initial values are permitted for $u(x, 0)$, subject only to the restriction that these values do not lie in the spinodal interval $[u_-^s, u_+^s]$ at any point whose distance from Γ_0 is greater than $O(\epsilon)$. At distances greater than $O(\epsilon)$, the derivatives will be presumed to be bounded independent of ϵ as ϵ tends to zero.

The main results of this paper are the following.

1. The internal structure of the transition layer is expected to stabilize in a time which is $O(\epsilon^2)$, and is measured on the timescale $T_2 = t/\epsilon^2$. The leading-order chemical potential within the transition layer should approach the value f_m , corresponding to phase equilibrium, on this timescale. After equilibration, the leading-order solution should be well described in terms of the well-known planar front profile $U(z)$, which is the unique solution of

$$F'(U) - \partial_z^2 U = f_m, \tag{1.6}$$

$$U(-\infty) = u_-^m, \quad U(+\infty) = u_+^m, \quad U(0) = \frac{1}{2}(u_-^m + u_+^m).$$

Here f_m, u_-^m, u_+^m must satisfy (see figure 1),

$$f_m = F'(u_-^m) = F'(u_+^m), \quad \int_{u_-^m}^{u_+^m} (F'(u) - f_m) du = 0.$$

Equation (1.3) has stationary planar front solutions of the form $U(\mathbf{x} \cdot \mathbf{m}/\epsilon)$ for any unit vector \mathbf{m} , representing coexistence of the two phases in equilibrium.

2. If the initial value of chemical potential at the interface deviates from phase equilibrium by an amount that is $O(1)$, then the leading-order outer solution contains a boundary layer. In the direction normal to the front, this layer should be described asymptotically for large values of T_2 (but small values of t) by a self-similar solution of the one-dimensional Stefan problem. The thickness of the boundary layer should be proportional to $\epsilon \sqrt{T_2} = \sqrt{t}$. Existence and uniqueness of the self-similar solution for affine $F'(u)$ is proved, including the delicate case when metastable states at infinity are permitted.

3. In the next slower stage of development, the outer solution at leading order formally should satisfy a nonlinear Stefan problem with the classical equilibrium condition at the interface. Interface motion is coupled to the leading order outer solution on this timescale. The leading-order solution is expected to approach a steady state at phase equilibrium. The interface in this steady state is formally arbitrary, determined dynamically from the initial conditions.

4. On the slowest timescale, $t_1 = \epsilon t$, phase equilibrium holds everywhere at leading order, and the normal velocity V of the interface is determined by the interfacial mean curvature κ according to the (non-local) law

$$V = [\mathbf{m} \cdot \nabla \mu_1]_{\pm}^+ / [U], \quad (1.7)$$

where μ_1 , the first-order term in the outer expansion of the chemical potential, is determined by solving the boundary value problems described by requiring that

$$\left. \begin{aligned} \Delta \mu_1 &= 0 && \text{in each phase away from the interface,} \\ \mu_1 &= -\kappa S / [U] && \text{on the interface,} \end{aligned} \right\} \quad (1.8)$$

and also a Neumann or Dirichlet-type boundary condition on the boundary of the domain. Here \mathbf{m} is a unit vector normal to the interface, $[\mathbf{m} \cdot \nabla \mu_1]_{\pm}^+$ is the jump in the normal derivative of μ_1 across the interface, $[U] = (u_{\mp}^m - u_{\pm}^m)$ is the jump in u across the interface at leading order, and $S = \int_{-\infty}^{\infty} U'(z)^2 dz$ is the coefficient of surface tension.

Physically, equation (1.8)₁ describes steady-state diffusion away from the interface, and (1.8)₂ is the Gibbs–Thompson condition for local equilibrium at the interface. Equations (1.7)–(1.8) turn out to be a well-known quasi-static model of front migration in solidification which can exhibit the Mullins–Sekerka shape instability. Further discussion of this model is in §7 below. In all likelihood, this régime is the one which is relevant during the late stages of phase separation by spinodal decomposition. During the early stages, a simple calculation of the wavelength of periodic perturbations of a homogeneous unstable state which have the maximal growth rate predicts that oscillatory spatial structures should be generated with a spatial size of order ϵ in a characteristic time of order ϵ^2 . In the time it takes for the structure to coarsen enough so that the assumptions here become valid, transients evolving on the faster scales described in (1)–(3) die away. But the description of the solution in régimes (1)–(3) does characterize the response of the solution to many perturbations. ‘Perturbations’ may be expected to occur frequently, in fact, as singularity formation, domain coalescence and domain collapse render the expansion invalid. The description in régime (3) can

also become invalid if interfacial instabilities cause the Stefan problem to be ill posed (cf. Sekerka 1983).

The method of matched asymptotic expansions has recently been applied to a number of problems involving migration of internal layers in phase transition problems. Caginalp & Fife (1988) use it to study a phase field model for solidification, obtaining a dynamic Gibbs–Thompson relation on the interface relating velocity, temperature and curvature. The present work is mostly built on the work of Rubinstein *et al.* (1989) who treat a non-conservative problem corresponding to the equation

$$u_t = \epsilon^2 \Delta u - F'(u) + f_m,$$

finding that on the slow timescale $\tau = \epsilon^2 t$, interface velocity is proportional to local mean curvature. This verifies the result of Allen & Cahn (1979) by a systematic formal mathematical method, by which errors can be assessed and corrections and modifications easily determined.

In the same sense, the present work clarifies some results of Kawasaki & Ohta (1982), who obtain a migration law resembling that in (4) above by more physical arguments. An early use of the nonlinear Cahn–Hilliard equation to discuss aspects of interface migration in one dimension was made by Langer & Sekerka (1975). Coutsias & Neu (1984) consider widely separated spherical interfaces, corresponding to a dilute suspension of droplets generated by a nucleation process. Gurtin (1988) has independently established a broad connection between equations of Cahn–Hilliard type and interface migration models of solidification and diffusion.

2. STABILIZATION OF THE TRANSITION LAYER

Considering initial data as specified above, let us develop an expansion for the solution, starting with the timescale $T_2 = t/\epsilon^2$. In this section and the next, a number of conjectures will have to be made about some interesting open problems which arise. I will suppose that in the domain $\Omega \subseteq \mathbb{R}^N$, there is a smooth $N-1$ dimensional front Γ , evolving in time, which divides Ω into regions Ω_+ and Ω_- so that $u > u_+^s$ in Ω_+ and $u < u_-^s$ in Ω_- at all points whose distance from the front is greater than $O(\epsilon)$. For convenience, I will assume that the front Γ does not intersect the boundary of the domain Ω .

First, consider the outer expansion far from the front. Seek an expansion in the form

$$u(x, t) = u_0 + \epsilon u_1 + \epsilon^2 u_2 + \dots, \tag{2.1}$$

$$\mu(x, t) = \mu_0 + \epsilon \mu_1 + \epsilon^2 \mu_2 + \dots, \tag{2.2}$$

where for $i = 0, 1, 2, \dots$,

$$u_i = u_i(x, T_2), \quad \mu_i = \mu_i(x, T_2), \quad T_2 = t/\epsilon^2.$$

Expanding the chemical potential in (1.2) in powers of ϵ , we find

$$\mu_0 = F'(u_0), \quad \mu_1 = F''(u_0) u_1, \quad \mu_2 = F''(u_0) u_2 + \frac{1}{2} F'''(u_0) u_1^2 - \Delta u_0. \tag{2.3}$$

From (1.3) follows

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

At leading order, nothing happens on the T_2 timescale; initial values are preserved. Initial values are also preserved at first order. Secular growth of the second-order term will ruin the validity of the leading term when $T_2 = O(\epsilon^{-2})$, however. That is, the first non-trivial timescale in the outer expansion is the scale $T_0 = t$, which will be considered in §4 below.

Now consider the inner expansion near the front. Introduce the stretched normal distance to the front,

$$z = \phi(x, T_2)/\epsilon,$$

where $\phi(x, T_2)$ is the signed distance from the point x in Ω to the front $\Gamma = \Gamma(T_2)$, such that $\phi > 0$ in Ω_+ , $\phi < 0$ in Ω_- . Near Γ , if Γ is smooth, then ϕ is smooth. Look for an expansion valid for x near Γ of the form

$$u(x, t) = \tilde{u}_0 + \epsilon \tilde{u}_1 + \epsilon^2 \tilde{u}_2 + \dots, \tag{2.4}$$

$$\mu(x, t) = \tilde{\mu}_0 + \epsilon \tilde{\mu}_1 + \epsilon^2 \tilde{\mu}_2 + \dots, \tag{2.5}$$

where for $i = 0, 1, 2, \dots$

$$\tilde{u}_i = \tilde{u}_i(z, x, T_2), \quad \tilde{\mu}_i = \tilde{\mu}_i(z, x, T_2), \quad T_2 = t/\epsilon^2.$$

It will be convenient to require that quantities depending on (z, x, T_2) are defined for x in a full neighbourhood of Γ , but do not change when x varies normal to Γ with z held fixed. If $w(z, x, T_2)$ is such a quantity, then $w(z, x, T_2) = w(z, x + \alpha \nabla \phi(x, T_2), T_2)$ for small real α , so $\nabla \phi(x, T_2) \cdot \nabla_x w(z, x, T_2) = 0$.

Define

$$\mathbf{m} = \nabla \phi(x, T_2), \quad \kappa = \Delta \phi(x, T_2) = \nabla \cdot \mathbf{m}, \quad V = \partial_{T_2} \phi(x, T_2). \tag{2.6}$$

When x lies on the front Γ , so $\phi(x, T_2) = 0$, then \mathbf{m} is the unit normal to Γ pointing toward Ω_+ , κ is the mean curvature of Γ at x (sum of principal curvatures), positive when the centre of curvature lies toward Ω_- , and V is the normal velocity of the front in the T_2 timescale, positive when the front moves toward Ω_- . Given $w(z, x, T_2)$ and $v(x, t) = w(\epsilon^{-1} \phi(x, t/\epsilon^2), x, t/\epsilon^2)$, derivatives appearing in (1.3) transform according to the relations

$$\left. \begin{aligned} \nabla v &= \nabla_x w + \epsilon^{-1} \mathbf{m} \partial_z w, \\ \Delta v &= \Delta_x w + \epsilon^{-1} \kappa \partial_z w + \epsilon^{-2} \partial_z^2 w, \\ \partial_t v &= \epsilon^{-2} \partial_{T_2} w + \epsilon^{-3} V \partial_z w. \end{aligned} \right\} \tag{2.7}$$

By using these equations, the expansions in (2.4) and (2.5) are related by

$$\left. \begin{aligned} \tilde{\mu}_0 &= F'(\tilde{u}_0) - \partial_z^2 \tilde{u}_0, \\ \tilde{\mu}_1 &= F''(\tilde{u}_0) \tilde{u}_1 - \partial_z^2 \tilde{u}_1 - \kappa \partial_z \tilde{u}_0, \\ \tilde{\mu}_2 &= F''(\tilde{u}_0) \tilde{u}_2 - \partial_z^2 \tilde{u}_2 - \kappa \partial_z \tilde{u}_1 + F'''(\tilde{u}_0) \tilde{u}_1^2/2 - \Delta_x \tilde{u}_0. \end{aligned} \right\} \tag{2.8}$$

A condition on \tilde{u}_i will be imposed to centre the front, defining a relation between Γ and the expansion, namely the condition

$$\int_{-\infty}^{\infty} U(z) (\tilde{u}(z, x, T_2) - U(z)) dz = 0, \tag{2.9}$$

where $\tilde{u} = \sum \epsilon^i \tilde{u}_i$ and the coefficient of each power of ϵ in (2.9) is required to vanish. This condition will prove particularly convenient to use in §§4 and 5 below. The

inner and outer expansions must also be related by matching conditions, which will be described in detail in §4.

It will be useful to allow the front to depend on ϵ on the timescale T_2 ; take $\phi = \phi(x, T_2, \epsilon)$ of the form

$$\phi = \phi_0(x, T_2) + \epsilon\phi_1(x, T_2). \tag{2.10}$$

Now expand (1.3) in powers of ϵ using (2.4), (2.5) and (2.7). The lowest-order terms are $O(\epsilon^{-3})$ and imply that $\partial_{T_2}\phi_0 = 0$, so to lowest order the front does not move on the T_2 timescale. Terms of order ϵ^{-2} in (1.3) yield

$$\partial_{T_2}\tilde{u}_0 + \partial_{T_2}\phi_1\partial_z\tilde{u}_0 = \partial_z^2(F'(\tilde{u}_0) - \partial_z^2\tilde{u}_0). \tag{2.11}$$

Changing the variable z to z_0 where $z_0 = z - \phi_1(x, T_2)$ gives the one-dimensional Cahn–Hilliard equation,

$$\partial_{T_2}\tilde{u}_0 = \partial_{z_0}^2(F'(\tilde{u}_0) - \partial_{z_0}^2\tilde{u}_0). \tag{2.12}$$

Boundary conditions for \tilde{u}_0 require that it match the outer solution when we take $z \rightarrow \pm\infty$ with $\epsilon z \rightarrow 0$:

$$\tilde{u}_0(z, x, T_2) \rightarrow \begin{cases} u_0^+(x) & \text{as } z \rightarrow \infty, \\ u_0^-(x) & \text{as } z \rightarrow -\infty, \end{cases} \tag{2.13}$$

where $u_0^+(x)$ (respectively $u_0^-(x)$) is the limit of $u_0(x, T_2)$ approaching x on Γ from Ω_+ (respectively Ω_-). I presume that $u_0^-(x) < u_-^s$ and $u_0^+(x) > u_+^s$, for all x on Γ , but that u_0^+ and u_0^- are otherwise arbitrary.

A rigorous analysis of the solution of (2.12) under the boundary conditions (2.13) is beyond the scope of the present paper. The solution of (2.12) cannot be expected to converge uniformly to a standing wave, because only one exists which connects the two different phases, namely $U(z_0)$ from (1.6), and this fails to satisfy the boundary conditions in (2.13) in general. Equation (2.12) does not admit travelling-wave solutions having the appropriate boundary conditions. The monotonic standing wave $U(z_0)$ is very likely to be stable, however (cf. Carr *et al.* 1984), so the following conjectures seem plausible:

For T_2 large, $\tilde{u}_0(z_0, x, T_2)$ should approach some translate $U(z_0 - \psi(x, T_2))$ of U in bounded intervals about the transition layer. The layer may move, but its velocity $\partial_{T_2}\psi$ will decrease toward zero as $T_2 \rightarrow \infty$. The values $U(\pm\infty) = u_{\pm}^m$, representing phase equilibrium, ‘propagate’ toward infinity by nonlinear diffusion, ultimately enforcing the boundary condition,

$$u_0^-(x) = u_-^m, \quad u_0^+(x) = u_+^m \quad \text{on } \Gamma, \tag{2.14}$$

on the outer solution on a slower timescale. This layer motion and diffusive propagation will be discussed in the next section.

3. BOUNDARY LAYER DEVELOPMENT

To describe the diffusive propagation of phase equilibrium into the outer expansion and complete the description of the inner expansion, expand the spatial scale. Fixing x on Γ , let $y = z_0/l(T_2)$, $\tau = \tau(T_2)$, and $w(y, \tau) = \tilde{u}_0(z_0, x, T_2)|_{z_0=y}l$. Then w satisfies

$$l^2\partial_{T_2}\tau\partial_\tau w - y l\partial_{T_2}l\partial_y w = \partial_y^2(F'(w) - l^{-2}\partial_y^2 w).$$

Choosing $l = \sqrt{2(T_2 + 1)}$, $\tau = \ln(T_2 + 1)$, w satisfies

$$2\partial_\tau w + \frac{1}{2}e^{-\tau}\partial_y^4 w = y\partial_y w + \partial_y^2 F'(w). \tag{3.1}$$

I conjecture that there is a unique real $y_*(x)$, determined by u_0^+ and u_0^- , such that the equation

$$0 = y\partial_y w + \partial_y^2 F'(w) \tag{3.2}$$

has a unique solution $W = W(y, x)$ in $(-\infty, y_*) \cup (y_*, \infty)$ with

$$\left. \begin{aligned} w(\infty) &= u_0^+(x), & w(-\infty) &= u_0^-(x), \\ w(y_* + 0) &= u_+^m, & w(y_* - 0) &= u_-^m, \end{aligned} \right\} \tag{3.3}$$

and satisfying the jump condition

$$0 = y_*(u_+^m - u_-^m) + \partial_y F'(w(y_* + 0)) - \partial_y F'(w(y_* - 0)). \tag{3.4}$$

The solution of equation (3.1) should approach $W(y)$ as $\tau \rightarrow \infty$. (As an aside, note that the function $W(x/\sqrt{2t})$ is a similarity solution of the two-phase nonlinear Stefan problem described in §4 below, in one dimension. For the case when $F'(u)$ is affine in each phase, existence and uniqueness of W will be proved in the Appendix.) The point y_* represents the scaled transition layer location; one expects $\psi(x, T_2) \sim y_*(x)\sqrt{2T_2}$ as $T_2 \rightarrow \infty$. Back in (2.11), we now expect that as $T_2 \rightarrow \infty$, $\tilde{u}_0(z, x, T_2) \sim U(z - \phi_1 - \psi)$ for bounded z . Recall that $\partial_{T_2} \phi_1$ represents the velocity (relative to the scales z, T_2) of the front Γ moving toward Ω_- , i.e. in the negative z -direction. To tie the inner expansion to the front location, impose the front centring condition (2.9) on the expansion. Assuming this condition holds at $T_2 = 0$, it continues to hold provided that

$$\partial_{T_2} \phi_1 = \frac{\int_{-\infty}^{\infty} U(z) \partial_z^2 (F'(\tilde{u}_0) - \partial_z^2 \tilde{u}_0) dz}{\int_{-\infty}^{\infty} U(z) \partial_z \tilde{u}_0 dz}. \tag{3.5}$$

This equation determines ϕ_1 . Because the front is centred, we expect $\tilde{u}_0(z, x, T_2) \rightarrow U(z)$ for $z = O(\sqrt{T_2})$ as $T_2 \rightarrow \infty$. Let us see how this can be consistent with $\psi \sim y_*\sqrt{2T_2}$. The denominator in (3.5) will approach $S = \int_{-\infty}^{\infty} U'(z)^2 dz$. For the numerator, the conjecture following (3.4) should imply that

$$\partial_z^2 (F'(\tilde{u}_0) - \partial_z^2 \tilde{u}_0) \sim -l^{-2}(z - \phi_1) \partial_z \tilde{u}_0,$$

so that approximately,

$$\partial_{T_2} \phi_1 \sim \frac{\phi_1 - c_1}{2(T_2 - 1)}, \quad c_1 = \int_{-\infty}^{\infty} zU'(z) dz/S.$$

It follows that $\phi_1 \sim c_2\sqrt{T_2}$ for large T_2 .

To sum up, the front motion on the T_2 timescale is expected to be determined by the relation $\phi_1(x, T_2) \sim y_*(x)\sqrt{2T_2}$ where $y_*(x)$ comes from the solution of the problem (3.2)–(3.4). The diffusion of the values $U(\pm\infty) = u_\pm^m$ into a boundary layer in the outer solution may be described by the approximation $\tilde{u}_0(z, x, T_2) \sim W(z/\sqrt{2T_2}, x)$, apparently valid for z between $O(1)$ and $o(\epsilon^{-1})$, T_2 between $O(1)$ and $o(\epsilon^{-2})$.

4. A STEFAN PROBLEM

Once the internal layer structure is equilibrated and the diffusive propagation described in the previous section is largely complete, further description of the solution of (1.3) must involve slower timescales. The next timescale which is appropriate is the scale $T_0 = t$. Consider first the outer expansion, made exactly as in (2.1)–(2.2), with the variable T_2 replaced by t . Expanding equation (1.3), we find that at leading order,

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

That is, $u_0(x, t)$ satisfies a standard diffusion equation. Because we expect the outer solution to avoid the spinodal interval, this equation might be expected to remain well posed under appropriate boundary conditions. On the outer boundary $\partial\Omega$, boundary conditions may be no flux (Neumann type)

$$\mathbf{n} \cdot \nabla \mu_0 = 0 \quad \text{on} \quad \partial\Omega, \tag{4.2}$$

or fixed potential (Dirichlet type)

$$u_0 = u_0^b, \quad \mu_0 = \mu_0^b = F'(u_0^b) \quad \text{on} \quad \partial\Omega. \tag{4.3}$$

Boundary conditions on the front Γ will be imposed from the inner expansion.

Next, make the inner expansion as in (2.4)–(2.5), replacing the variable T_2 by t . Here it will not be necessary to allow $\phi(x, t)$ to depend on ϵ to the order considered. Expanding (1.3), we find that the lowest-order terms yield

$$0 = \partial_z^2 \tilde{\mu}_0 = \partial_z^2 (F'(\tilde{u}_0) - \partial_z^2 \tilde{u}_0) \tag{4.4}$$

$$V \partial_z \tilde{u}_0 = \partial_z^2 \tilde{\mu}_1 + \kappa \partial_z \tilde{\mu}_0 \tag{4.5}$$

where $V(x, t) = \partial_t \phi(x, t)$ is the velocity of the front for x on Γ . To determine the leading term, integrate (4.4). For some $a_0(x, t)$, $b_0(x, t)$, we must have

$$F'(\tilde{u}_0) - \partial_z^2 \tilde{u}_0 = a_0 z + b_0. \tag{4.6}$$

Since \tilde{u}_0 must remain bounded as $z \rightarrow \pm\infty$, we must have $a_0 = 0$. We require that the phase changes across the interfacial zone, so $\tilde{u}_0 > u_+^s$ for $z \gg 0$, $\tilde{u}_0 < u_-^s$ for $z \ll 0$. By phase plane analysis of equation (4.6) it is easy to see that a solution can be found if and only if $b_0 = f_m = F'(u_\pm^m)$. The solution is some translate of the standing wave from (1.6); $\tilde{u}_0(z, x, t) = U(z + \alpha(x, t))$. To identify which translate, impose the front centring condition (2.9). It follows that

$$\tilde{u}_0(z, x, t) = U(z), \quad \tilde{\mu}_0(z, x, t) = f_m. \tag{4.7}$$

Matching this result to the outer expansion, one obtains the classical equilibrium boundary condition

$$u_0^+(x, t) = U(\infty) = u_+^m, \quad u_0^-(x, t) = U(-\infty) = u_-^m \quad \text{on} \quad \Gamma. \tag{4.8}$$

For further progress, the matching conditions for the inner and outer expansions of the chemical potential must be developed. In general, these are obtained as

follows (cf. Caginalp & Fife 1988). Fixing x on Γ , we seek to match the expansions by requiring formally that

$$(\mu_0 + \epsilon\mu_1 + \dots)(x + \epsilon z\mathbf{m}, t) \approx (\tilde{\mu}_0 + \epsilon\tilde{\mu}_1 + \dots)(z, x, t)$$

when ϵz is between $O(\epsilon)$ and $o(1)$. Expand the left-hand side in powers of ϵ as $\epsilon z \rightarrow 0+$, obtaining

$$\mu_0^+ + \epsilon(\mu_1^+ + zD_m\mu_0^+) + \epsilon^2(\mu_2^+ + zD_m\mu_1^+ + \frac{1}{2}z^2D_m^2\mu_0^+) + \dots,$$

where D_m denotes the directional derivative along \mathbf{m} , and

$$\mu_i^+(x, t) = \lim_{s \rightarrow 0+} \mu_i(x + s\mathbf{m}, t), \text{ etc.}$$

A similar expansion is obtained for $\epsilon z \rightarrow 0-$. To match these expansions to the inner expansion, one requires that

$$\left. \begin{aligned} \mu_0^\pm(x, t) &= \lim_{z \rightarrow \pm\infty} \tilde{\mu}_0(z, x, t), \\ (\mu_1^\pm + z\mathbf{m} \cdot \nabla\mu_0^\pm)(x, t) &= \tilde{\mu}_1(z, x, t) + o(1) \quad \text{as } z \rightarrow \pm\infty, \\ (\mu_2^\pm + z\mathbf{m} \cdot \nabla\mu_1^\pm + \frac{1}{2}z^2D_m^2\mu_0^\pm)(x, t) &= \tilde{\mu}_2(z, x, t) + o(1) \quad \text{as } z \rightarrow \pm\infty. \end{aligned} \right\} \quad (4.9)$$

By using these matching conditions, we can now relate the front velocity to the expansion. Integrating (4.5) in z , and using the matching condition (4.9)₂, it follows that

$$V(x, t) = [U]^{-1} [\mathbf{m} \cdot \nabla\mu_0]^\pm. \quad (4.10)$$

where $[U] = u_+^m - u_-^m$, and $[\mathbf{m} \cdot \nabla\mu_0]^\pm = \mathbf{m} \cdot \nabla\mu_0^+ - \mathbf{m} \cdot \nabla\mu_0^-$. Equations (4.1)–(4.3), (4.8) and (4.10), together with the initial conditions, should determine the motion of the front and the diffusion of the concentration on this timescale. One might expect the solution to approach a stationary state as t becomes large. Under no-flux boundary conditions, or if (4.3) holds with $\mu_0^b = f_m$, stationary states may be obtained with an *arbitrary* front Γ , taking $u_0(x) = u_+^m$ in Ω_+ , $u_0(x) = u_-^m$ in Ω_- . Once some such state is approached for large t , the front should continue to evolve on the slower timescale $t_1 = \epsilon t$ as described in §5 below.

This discussion may be wrongheaded in general. Formally, metastable states have been permitted here on either or both sides of the front. But in this case it seems likely (cf. Sekerka 1983) that short-wavelength interfacial instabilities would render the approximation invalid, or cause the problem in (4.1)–(4.3), (4.8) and (4.10) to become ill posed.

5. NON-LOCAL INTERFACE MIGRATION BY CURVATURE

Supposing the solution has equilibrated on the $O(1)$ timescale, now consider evolution on the slower timescale $t_1 = \epsilon t$. In this section, consider only the no-flux (Neumann-type) boundary conditions (1.4); the fixed-potential (Dirichlet-type) conditions (1.5) are discussed in the next section. The outer expansion is made

exactly as in (2.1)–(2.2), with the variable T_2 replaced by t_1 . The relations (2.3) hold. Expanding equation (1.3) and matching powers of ϵ , we require

$$\left. \begin{aligned} 0 &= \Delta\mu_0 = \Delta F'(u_0), \\ \partial_{t_1} u_0 &= \Delta\mu_1 = \Delta F''(u_0) u_1, \\ \partial_{t_1} u_1 &= \Delta\mu_2 = \Delta(F''(u_0) u_2 + \frac{1}{2}F'''(u_0) u_1^2 - \Delta u_0). \end{aligned} \right\} \quad (5.1)$$

We expect $F''(u_0) > 0$ away from the front, so these equations will be well-posed elliptic equations to solve for u_0, u_1 , etc., in turn, in each component of Ω_+ and Ω_- separately. To do this, boundary conditions for μ_0, μ_1 , etc., are needed. On the fixed boundary $\partial\Omega$, the boundary condition (1.4) yields

$$\nabla\mu_i \cdot \mathbf{n} = 0 \quad \text{on} \quad \partial\Omega, \quad i = 0, 1, \dots \quad (5.2)$$

Next, make an inner expansion exactly as in (2.4)–(2.5), again replacing T_2 with t_1 . Note that the front velocity $V = \partial_{t_1} \phi(x, t_1)$ is measured with respect to the slow timescale, and equation (2.7)₃ is replaced by

$$\partial_t v = \epsilon \partial_{t_1} w + V \partial_z w. \quad (5.3)$$

The relations (2.8) hold as before, so by expanding equation (1.3), we have

$$\left. \begin{aligned} 0 &= \partial_z^2 \tilde{\mu}_0, \\ 0 &= \partial_z^2 \tilde{\mu}_1 + \kappa \partial_z \tilde{\mu}_0, \\ V \partial_z \tilde{\mu}_0 &= \partial_z^2 \tilde{\mu}_2 + \kappa \partial_z \tilde{\mu}_1 + \Delta_x \tilde{\mu}_0. \end{aligned} \right\} \quad (5.4)$$

Boundary conditions for these equations will come from the matching conditions. The leading term in the inner expansion is determined exactly as in §4; the transition layer is at equilibrium, with

$$\tilde{u}_0(z, x, t_1) = U(z), \quad \tilde{\mu}_0(z, x, t_1) = f_m. \quad (5.5)$$

Matching this to the outer expansion gives the boundary condition on the front for the leading-order term;

$$\mu_0 = f_m \quad \text{on} \quad \Gamma. \quad (5.6)$$

By using the boundary condition (5.2), it follows that the leading term is at phase equilibrium everywhere, with

$$\mu_0 = f_m \quad \text{in} \quad \Omega, \quad u_0(x, t_1) = u_+^m \quad \text{in} \quad \Omega_+, \quad u_-^m \quad \text{in} \quad \Omega_-. \quad (5.7)$$

Now consider the next order in the expansion. From (5.4)₂, for some $a_1(x, t_1), b_1(x, t_1)$ we must have

$$F''(U) \tilde{u}_1 - \partial_z^2 \tilde{u}_1 = \kappa U'(z) + a_1 z + b_1. \quad (5.8)$$

To determine a_1 , which equals $\partial_z \tilde{\mu}_1(z, x, t_1)$, use the matching condition (4.9)₂. It follows that $a_1(x, t_1) = 0$. To determine b_1 , observe that from (1.6) it follows that

$$F''(U) U' - \partial_z^2 U' = 0. \quad (5.9)$$

Multiply equation (5.8) by U' and integrate in z from $-\infty$ to ∞ . By (5.9) the left-hand side must vanish, and we find that

$$\tilde{\mu}_1(z, x, t_1) = -\kappa(x, t_1)S[U]^{-1}, \quad \text{where} \quad S = \int_{-\infty}^{\infty} U'(z)^2 dz. \quad (5.10)$$

Then $\tilde{u}_1 = \kappa(x, t_1)U_1(z)$, where $U_1(z)$ is the unique bounded solution of

$$F''(U)U_1 - \partial_z^2 U_1 = U'(z) - S[U]^{-1}$$

which satisfies $\int_{-\infty}^{\infty} U'(z)U_1(z) dz = 0$.

Equation (5.10) yields boundary conditions for the first-order term μ_1 in the outer expansion of the chemical potential. Thus this term is determined from the problem

$$\left. \begin{aligned} \Delta\mu_1 &= 0 && \text{in } \Omega_+ \text{ and } \Omega_-, \\ \mu_1 &= -\kappa(x, t_1)S[U]^{-1} && \text{on } \Gamma, \\ \mathbf{n} \cdot \nabla\mu_1 &= 0 && \text{on } \partial\Omega. \end{aligned} \right\} \quad (5.11)$$

Physically, at first order one has steady state diffusion in the outer expansion, and the Gibbs–Thompson equilibrium condition holds on the interface. If Γ is smooth and known, (5.11) forms a well-posed problem which may be solved separately in each connected component of Ω_+ and Ω_- .

The front velocity is determined at the next order in the expansion. From (5.4)₃, we require $VU'(z) = \partial_z^2 \tilde{\mu}_2$. Integrate in z from $-\infty$ to ∞ and use the matching condition in (4.9)₃. One finds that for x on Γ ,

$$V(x, t_1) = [\mathbf{m} \cdot \nabla\mu_1(x, t_1)]^{\pm}[U]^{-1}. \quad (5.12)$$

Physically, the front motion is due to the mismatch of mass flux induced by the solution of (5.11). The system (5.11)–(5.12) should constitute a well-posed problem to determine the motion of the front, given smooth initial conditions. The current configuration of the front determines μ_1 through the boundary conditions in (5.11), and this determines the velocity in (5.12). The relation between front curvature and velocity is non-local; a discussion appears in §7.

6. DIRICHLET-TYPE BOUNDARY CONDITIONS

In this section I describe how the treatment in §5 is modified for the fixed potential (Dirichlet type) boundary conditions in (1.5). The discussion here includes the case $\Omega = \mathbb{R}^N$ where the state at infinity is uniform. I suppose throughout that the front Γ does not meet $\partial\Omega$. For definiteness, assume that $\partial\Omega$ forms part of the boundary of Ω_+ , and does not meet the boundary of Ω_- . Suppose the boundary conditions take the form

$$\left. \begin{aligned} \mu &= \mu_0^b + \epsilon\mu_1^b + \epsilon^2\mu_2^b + \dots \\ u &= u_0^b + \epsilon u_1^b + \epsilon^2 u_2^b + \dots \end{aligned} \right\} \quad \text{on } \partial\Omega, \quad (6.1)$$

where μ_i^b and u_i^b are constants. This permits one to consider states that are just slightly metastable at infinity, for example.

The outer expansion is made the same as in §5, with the same result as in (5.1), but with the boundary conditions in (5.2) replaced by

$$\mu_i = \mu_i^b, \quad u_i = u_i^b \quad \text{on} \quad \partial\Omega, \quad i = 0, 1, \dots \tag{6.2}$$

For the inner expansion, one obtains equations (5.4) as before, and finds that equilibrium holds at leading order as before, so that (5.5) holds, and (5.6) gives the boundary values for the leading-order term in the outer expansion.

Now it seems that the solution for μ_0 may differ from that in §5 if $\mu_0^b \neq f_m$. One may find μ_0 by solving the Dirichlet problem posed by (5.1)₁ in Ω_+ and Ω_- with the boundary conditions in (5.6) and (6.2). By the maximum principle, the solution takes its values between f_m and μ_0^b . Provided $\mu_0^b > F'(u_+^s)$, one may continuously invert the relation $\mu_0 = F'(u_0)$ to find u_0 in Ω_+ with $u_0 > u_+^s$. On components of Ω_+ that do not meet $\partial\Omega$, and on Ω_- , the leading-order term is constant as before, with $\mu_0 = f_m$, $u_0 = u_+^m$ or u_-^m .

But, I claim, this expansion on the timescale $t_1 = \epsilon t$ is not valid, unless

$$\mu_0^b = f_m. \tag{6.3}$$

To determine the order ϵ terms, one must solve (5.4)₂ with boundary conditions that come from the matching condition (4.9)₂. One must have $\partial_z \tilde{\mu}_1 = a_1$ independent of z , so it follows that

$$[\mathbf{m} \cdot \nabla \mu_0(x, t_1)]_{\pm}^{\pm} = 0.$$

But $\mu_0 = f_m$ in Ω_- , so $\mathbf{m} \cdot \nabla \mu_0 = 0$ on Γ . Combining this as a boundary condition with $\mu_0 = \mu_0^b$ on $\partial\Omega$, it follows that $\mu_0 = \mu_0^b$ everywhere in Ω_+ . Then (6.3) must hold. As before, we conclude that the leading-order terms rest at phase equilibrium; (5.7) holds.

The determination of $\tilde{\mu}_1$ and \tilde{u}_1 proceeds exactly as in §5, yielding (5.10). This provides boundary conditions for μ_1 , so that μ_1 is the solution of the Dirichlet problem

$$\left. \begin{aligned} \Delta \mu_1 &= 0 \quad \text{in} \quad \Omega_+ \quad \text{and} \quad \Omega_-, \\ \mu_1 &= -\kappa(x, t_1) S[U]^{-1} \quad \text{on} \quad \Gamma, \\ \mu_1 &= \mu_1^b \quad \text{on} \quad \partial\Omega. \end{aligned} \right\} \tag{6.4}$$

The next order in the expansion behaves as in §5. Equation (5.12) must hold, giving the normal velocity of the front in terms of the solution of (6.4).

7. DISCUSSION

Migration of simple fronts under the velocity law (5.11)–(5.12) has been considered by several authors, primarily with regard to solidification theory. See the paper of Gurtin (1986) who refers to several other works and review articles. Mullins & Sekerka (1963) argued that a single sphere in \mathbb{R}^3 , growing according to the law implied by (6.4) and (5.12) with $\mu_1^b < 0$, becomes linearly unstable to non-radial perturbations when the radius exceeds a (rather small) critical value. In this case the state at infinity is slightly metastable. Duchon & Robert (1984) established existence and uniqueness locally in time for a single closed loop in the

plane with two L_2 derivatives evolving according to equations like (5.11)–(5.12), but neglecting diffusion exterior to the loop.

Gurtin (1986) develops several properties of fronts smoothly evolving under the migration law (5.11)–(5.12) and many related ones. For clarity's sake, let me specialize some of his arguments to the present case. Let $\text{vol } \Omega_{\pm}$ denote the N -dimensional volume, and let $\text{area } \Gamma$ denote the $(N-1)$ -dimensional area of the front. As before, suppose that Ω_- does not meet $\partial\Omega$.

THEOREM. *Suppose the front Γ is smoothly evolving according to (5.12).*

(a) *If (5.11) holds (no-flux boundary conditions), then*

$$d \text{vol } \Omega_+ / dt_1 = d \text{vol } \Omega_- / dt_1 = 0, \quad (7.1)$$

and

$$\frac{d}{dt_1} (S \cdot \text{area } \Gamma) = - \int_{\Omega} |\nabla \mu_1|^2 \leq 0. \quad (7.2)$$

(b) *If (6.4) holds (fixed potential boundary conditions), then*

$$\frac{d}{dt_1} (S \cdot \text{area } \Gamma + \mu_1^b [U] \text{vol } \Omega_-) = - \int_{\Omega} |\nabla \mu_1|^2 \leq 0. \quad (7.3)$$

Proof. Let me begin from the basic formulae (cf. Gurtin 1986)

$$\frac{d}{dt_1} \text{vol } \Omega_- = - \int_{\Gamma} V, \quad \frac{d}{dt_1} \text{area } \Gamma = - \int_{\Gamma} \kappa V. \quad (7.4)$$

Recall that $V = [\mathbf{m} \cdot \nabla \mu_1]_{-}^{+} [U]^{-1}$. Let \mathbf{n}_+ and \mathbf{n}_- denote the outward unit normals to Ω_+ and Ω_- respectively. On Γ , $\mathbf{n}_- = \mathbf{m}$ and $\mathbf{n}_+ = -\mathbf{m}$. Let $\nabla \mu_1^+$ and $\nabla \mu_1^-$ denote the limiting values of $\nabla \mu_1$ on Γ from the interior of Ω_+ and Ω_- respectively. On Γ , we have $[\mathbf{m} \cdot \nabla \mu_1]_{-}^{+} = -\mathbf{n}_+ \cdot \nabla \mu_1^+ - \mathbf{n}_- \cdot \nabla \mu_1^-$. Now

$$[U] \frac{d}{dt_1} \text{vol } \Omega_- = \int_{\partial\Omega_+} \mathbf{n}_+ \cdot \nabla \mu_1^+ + \int_{\partial\Omega_-} \mathbf{n}_- \cdot \nabla \mu_1^- - \int_{\partial\Omega} \mathbf{n} \cdot \nabla \mu_1 = - \int_{\partial\Omega} \mathbf{n} \cdot \nabla \mu_1, \quad (7.5)$$

by using the divergence theorem and the fact that $\Delta \mu_1 = 0$ in Ω_+ and Ω_- . In (a), the last term vanishes, yielding (7.1).

Next, recall that on Γ , $\mu_1 = -\kappa S [U]^{-1}$, so we have

$$\begin{aligned} \frac{d}{dt_1} (S \cdot \text{area } \Gamma) &= \int_{\Gamma} \mu_1 [\mathbf{m} \cdot \nabla \mu_1]_{-}^{+} \\ &= \int_{\partial\Omega_+} \mu_1 \mathbf{n}_+ \cdot \nabla \mu_1^+ + \int_{\partial\Omega_-} \mu_1 \mathbf{n}_- \cdot \nabla \mu_1^- - \int_{\partial\Omega} \mu_1 \mathbf{n} \cdot \nabla \mu_1 \\ &= - \int_{\Omega} |\nabla \mu_1|^2 + \int_{\partial\Omega} \mu_1 \mathbf{n} \cdot \nabla \mu_1. \end{aligned} \quad (7.6)$$

again by using the divergence theorem and that $\Delta \mu_1 = 0$ in Ω_+ and Ω_- . By using the boundary condition in (6.4), the results (7.2) and (7.3) follow. For the case of unbounded Ω , consult Gurtin (1986).

As discussed by Gurtin, because of (7.2) it seems reasonable to expect that under no-flux boundary conditions, a stable equilibrium interface should have minimal

area with $\text{vol } \Omega_-$ held constant, hence will have constant mean curvature, meeting $\partial\Omega$ orthogonally. Under fixed potential boundary conditions, the interface should vanish at equilibrium, with $\Omega = \Omega_+$ if $\mu_1^b > 0$, $\Omega = \Omega_-$ if $\mu_1^b < 0$, either case possible if $\mu_1^b = 0$.

More generally, under no-flux boundary conditions, any interface of constant mean curvature is stationary. (The converse is not clear.) Thus, for example, a collection of spheres of equal radius, positions arbitrary, is stationary. But increasing the radius of one sphere while decreasing another, with constant total volume, the total area decreases, so such a collection is unstable.

8. SUMMARY

The formal calculations presented here offer evidence that the nonlinear Cahn–Hilliard equation may be considered a regularization of both the nonlinear Stefan problem described in §4 and, on the timescale $t_1 = \epsilon t$, the quasi-static solidification model (5.11)–(5.12). The results support the notion that the nonlinear Cahn–Hilliard equation gives a qualitatively correct description of both early and late stages of phase separation by spinodal decomposition.

The treatment presented here is limited in several ways. I have not considered any short length scales tangent to the interface, so have not treated the important issue of how fronts intersect boundaries, nor that of how short-wave instabilities arising in the Stefan problem might evolve. The early stages of coarsening after spinodal decomposition and the processes of domain coalescence and disappearance are beyond the range of formal validity of the expansion. Finally, I have not attempted to explain the dynamic scaling of the structure factor which is observed in experiments and computations, choosing to focus on the detailed laws of motion that govern the interface.

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APPENDIX A. SIMILARITY SOLUTIONS OF THE TWO PHASE STEFAN PROBLEM

As remarked in the discussion of §3 on boundary layer development, a solution $W(y)$ of equations (3.2)–(3.4) yields a similarity solution to the two-phase Stefan problem posed by (4.1), (4.8) and (4.10) in one dimension. For the case when $F'(u)$ is affine in each phase, similarity solutions are discussed by Carslaw & Jaeger (1959) and by Crank (1984), following F. Neumann. Proofs of existence and uniqueness do not seem to be available, however, and when the boundary conditions at infinity involve metastable states, the proof involves some careful estimates. Therefore it seems worthwhile to present a proof. In the result below, the boundary values permitted are quite general; either or both phases may be metastable at infinity. Such solutions are very likely to be unstable in more than

one space dimension, however. The weak restrictions on boundary values in (A 1) arise naturally in the proof and amount to requiring that $F'(u)$ be single valued.

THEOREM. *Suppose that $a_{\pm} > 0$ and that*

$$u_0^- < u_+^m, \quad u_0^- < u_0^+, \quad u_-^m < u_0^+. \tag{A 1}$$

Then there exists a unique real z such that the problem

$$\begin{aligned} yu_y + a_+^2 u_{yy} &= 0 \quad \text{in } (z, \infty) \quad \text{with } u(z+) = u_+^m, \quad u(\infty) = u_0^+, \\ yu_y + a_-^2 u_{yy} &= 0 \quad \text{in } (-\infty, z) \quad \text{with } u(z-) = u_-^m, \quad u(-\infty) = u_0^-, \\ z(u_+^m - u_-^m) + (a_+^2 u_y(z+) - a_-^2 u_y(z-)) &= 0 \end{aligned}$$

has a solution.

Proof. It is straightforward to show that any solution of the problem in question must have the classical Neumann form

$$\begin{aligned} u(y) &= u_0^- + (u_-^m - u_0^-) \alpha(y/a_-) / \alpha(z/a_-) \quad \text{for } y \text{ in } (-\infty, z), \\ u(y) &= u_0^+ + (u_+^m - u_0^+) \alpha(-y/a_+) / \alpha(-z/a_+) \quad \text{for } y \text{ in } (z, \infty), \end{aligned}$$

where $\alpha(y) = \int_{-\infty}^y \exp(-t^2/2) dt$, and that these formulae yield a solution to the problem if and only if $0 = H(z)$ where

$$H(z) = z + \gamma_+ a_+ (\alpha'/\alpha)(-z/a_+) - \gamma_- a_- (\alpha'/\alpha)(z/a_-),$$

with γ_+ and γ_- defined by

$$\gamma_+ = (u_0^+ - u_+^m) / (u_+^m - u_-^m), \quad \gamma_- = (u_-^m - u_0^-) / (u_+^m - u_-^m).$$

The conditions in (A 1) hold if and only if

$$\gamma_+ > -1, \quad \gamma_- > -1 \quad \text{and} \quad \gamma_+ + \gamma_- > -1. \tag{A 2}$$

Metastable phases correspond to negative values of γ_+ or γ_- . I claim that if the conditions (A 2) hold, then we have

$$H'(z) > 0 \quad \text{for all } z, \quad \text{and} \quad \lim_{z \rightarrow \pm\infty} H'(z) = 1 + \gamma_{\pm} > 0,$$

which implies that $H(z)$ has a unique zero. This claim follows directly from the following lemma, which also implies that $\ln \alpha(y)$ is concave.

LEMMA. *Define $\beta(y) = (\alpha'/\alpha)'(y)$, so $\beta(y) = -(y\alpha\alpha' + \alpha'^2)/\alpha^2$. Then $-1 < \beta(y) < 0$ for all y .*

Proof. Consider first $y \geq 0$. Clearly $\beta < 0$. Because $\beta(\infty) = 0$ and $\beta(0) = -2/\pi$ lies in $(-1, 0)$ and $(\alpha^2(1+\beta))' = (1+y)^2\alpha\alpha' + y\alpha'^2 > 0$ for $y > 0$, we have $\alpha^2(1+\beta) > 0$, hence $\beta > -1$ for all $y \geq 0$.

For $y < 0$, define $\omega(y) = \alpha'(y)/y\alpha(y)$. Then $\omega < 0$, and $\beta = -y^2\omega(1+\omega)$. Clearly $\lim_{y \rightarrow 0^-} \omega(y) = -\infty$, and it is not difficult to show using l'Hôpital's rule that

$$\lim_{y \rightarrow -\infty} \omega(y) = -1, \quad \lim_{y \rightarrow -\infty} y^2(1+\omega) = -1.$$

Then since $(\alpha(1+\omega))' = -\alpha'/y^2 < 0$, it follows that $1+\omega < 0$ for all $y < 0$. We obtain

$$\beta < 0 \quad \text{and} \quad \lim_{y \rightarrow -\infty} \beta(y) = -1.$$

Now, $1+\beta(0) > 0$, and because

$$y^2(1+\beta) = y^2(1+y^2(1+\omega)) - y^4(1+\omega)^2 = [(y^4+y^2)\alpha + y^3\alpha']/\alpha - (y^2(1+\omega))^2,$$

we find that $\lim_{y \rightarrow -\infty} y^2(1+\beta) = \lim_{y \rightarrow -\infty} 4y^2(1/\omega + 1) + 2/\omega - 1 = 1$. Hence $1+\beta > 0$ for large negative y . Now $1+\beta > 0$ if and only if $\alpha^2(1+\beta) > 0$. To prove that $\alpha^2(1+\beta) > 0$, it is enough to show that $(\alpha^2(1+\beta))' \neq 0$ for $y < 0$. Define

$$G(y) = (\alpha^2(1+\beta))'/[(1+y^2)\alpha'] = \alpha + y\alpha'/(1+y^2).$$

Then $G(0) > 0$ and $\lim_{y \rightarrow -\infty} y^2(1+y^2)G/\alpha = \lim_{y \rightarrow -\infty} y^2(1+y^2(1+\omega)) = 2$, so $G(y) > 0$ for all y . Hence $\beta > -1$ for all $y < 0$, and the lemma is proved.

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