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PHASE FIELD MODELS AND SHARP INTERFACE LIMITS: SOME DIFFERENCES IN SUBTLE SITUATIONS

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1. Introduction. We discuss a system of equations which has been investigated extensively [**1**–**25**]. In this article we compare this approach with various macroscopic formulations obtained as modifications of Stefan problems and indicate critical situations in which the two approaches differ. The crux of this approach involves an "order" parameter, ϕ, which is coupled to the temperature, u, but is not simply dependent on it. Such a function ϕ can be expected to be a minimizer of the free energy such as

$$\mathcal{F}\{\phi\} = \int_\Omega dx\{\xi^2(\nabla\phi)^2 + \frac{1}{8a}(\phi - \phi^3) - 2u\phi\} \tag{1.1}$$

if the material occupies a region Ω and is in equilibrium. This is a consequence of a statistical mechanical analysis of a phase transition [**25**]. If the system is not in equilibrium, or in a steady-state, the free energy will no longer be a minimum, but will satisfy $\tau\phi_\tau = -\delta\mathcal{F}/\delta\phi$. The microscopic parameters τ, ξ can be related to macroscopically measurable quantities.

Coupled with a heat conservation equation which incorporates the latent heat of fusion, one then has the system, for any symmetric double-well potential $G(\phi)$ with minima at ± 1,

$$u_t + \frac{l}{2}\phi_t = K\Delta u \tag{1.2}$$

$$\tau\phi_t = \xi^2\Delta\phi + \frac{1}{2a}G'(\phi) + 2u \tag{1.3}$$

subject to appropriate initial and boundary conditions, e.g.,

$$u(0,x) = u_0(x), \qquad \phi(0,x) = \phi_0(x), \qquad x \in \Omega \tag{1.4}$$

$$u(t,x) = u_\partial(x), \qquad \phi(t,x) = \phi_\partial(x), \qquad x \in \Omega. \tag{1.5}$$

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Further discussion of the physical derivation may be found in [**1**,**8**].

The interface in the problem (1.2), (1.3) is not defined by the temperature directly as in the Stefan model (see Section 3) but consists of the points

$$\Gamma(t) = \{x \in \Omega : \phi(t,x) = 0\}. \tag{1.6}$$

In fact, the macroscopic condition which relates the temperature, velocity, curvature and surface tension at the interface can be derived (see Section II) directly from (1.2), (1.3) since the appropriate physics has already been incorporated into the free energy (1.1).

The questions of existence, uniqueness and regularity have been considered [**1**] for (1.2)–(1.5). Suppose for simplicity that $G(\phi) = \phi - \phi^3$ and $a = 1$. Using the standard metric

$$d(P,Q) \equiv \{|x_1 - x_2|^2 + |t_1 - t_2|\}^{1/2} \tag{1.7}$$

where $P = (t_1, x_1)$, $Q = (t_2, x_2)$ in $\Lambda \equiv \overline{\Omega} \times [0,T]$ on the Banach space $C_{2+\alpha}(\Lambda)$ with $\alpha \in (0,1)$ one has

Theorem (Existence, uniqueness and regularity). *Suppose that c_1, l, K, ξ and τ are any set of positive constants subject to*

$$c_1 \leq \xi^2/\tau \leq K. \tag{1.8}$$

If the initial and boundary data (1.4), (1.5) *are in $C_{2+\alpha}$, then there exists a solution (u,ϕ) to* (1.2)–(1.5) *in $C_{2+\alpha}$. Furthermore, one has the bounds*

$$\left|\frac{\partial \phi}{\partial (x/\xi)}\right| \leq c, \qquad \left|\frac{\partial^2 \phi}{\partial (x/\xi)^2}\right| \leq c \tag{1.9}$$

where c is a constant which depends on $l, K, \Omega, T, u_0, u_\partial, \phi_0, \phi_\partial$ and c_1, but not on ξ or τ.

The significance of the bounds (1.9) is that, for small ξ, an interface of thickness ξ does not become appreciably sharper in time.

For the time independent problem several variational analyses have been implemented. In particular some general results were presented

in [**1**, p. 241] based on methods of [**3**]. Recently, the problem has also been considered in terms of global minimizers and Γ convergence [**2**]. These ideas have been further pursued in [**27**].

2. Relation at interface. A natural question which arises for equations (1.2), (1.3) is the temperature at the interface Γ. The boundary conditions (1.5) must be chosen so that ϕ makes a transition and that it does so as an internal layer. Otherwise, Γ may be the empty set (e.g., for Neumann boundary conditions) or it may be within $O(\xi)$ of the external boundary (e.g., if the temperature is too large or too small). The geometry of Ω now also becomes relevant since the curve Γ will either be a closed curve or it will intersect with the external boundary, $\partial\Omega$. The latter case involves a physical understanding of the interaction between each of the two phases and the container, in addition to the physics of the interface which has been incorporated into (1.1). Hence, one way of restricting the problem to one which is within the bounds of the physical assumptions of the problem is to consider an annular region. This is also a natural geometry for crystal growth.

These issues are also naturally separated into the time-independent (steady state or equilibrium) and the time-dependent problems. A number of rigorous results have been obtained for the steady-state situation. The first work of this type ([**1**, Sections 4–7], see also [**4**–**6**]), involved a rigorous asymptotic expansion to all orders about a fixed interface, Γ. With surface tension, σ, calculated from (1.1) as $2/3\xi$ and change in entropy between phases as $\Delta s = 4$, the asymptotic expression

$$\Delta s u(x) = -\sigma\kappa(x) + O(\xi^2), \qquad x \in \Gamma \tag{2.1}$$

then follows as a necessary condition with $\kappa(x)$ defined as the sum of principal curvatures. This confirms a classical result known as the Gibbs-Thomson condition [**22**].

Note that in the time-independent case equation (1.2) reduces to $\Delta u = 0$, so that u is determined entirely by the boundary conditions. Equation (1.3) then becomes

$$0 = \xi^2\Delta\phi + \frac{1}{2}(\phi - \phi^3) + 2u \tag{2.2}$$

subject to boundary conditions $\phi = \phi_- \simeq -1$ in the interior (solid) and $\phi = \phi_+ \simeq +1$ in the exterior (liquid). The boundary conditions on u are assumed to be $\mathcal{O}(\xi)$.

In order to establish the sufficiency of this condition one must prove the existence of layered solutions to (2.2) subject to the boundary conditions above. We note that constant boundary conditions for u imply constant u, which must balance the sum of principal curvatures term. In particular, in two dimensions constant temperature means constant radius of curvature.

For constant temperatures, then, it is reasonable to look for internal layers in spherically symmetric annular regions in $\mathbf{R}^n$. These questions were investigated in two papers [**18,20**] using shooting methods, the maximum principle and Green's functions. In particular, it has been proven that there exists a solution to (2.2) and that any solution must have a transition layer at the radius, r, for which (2.1) is valid. This means that, while there is no assertion of uniqueness, the solutions must nevertheless be in a narrow band of width of order ξ.

The case of nonspherically symmetric geometries was subsequently considered [**12,13**] in two-dimensional space. A preliminary problem which was resolved is the following. Given a smooth function $u(x)$, defined in an annular region, does there exist a curve Γ such that

$$4u(x) = -\sigma\kappa(x) \tag{2.3}$$

for all points x on Γ? Under suitable conditions on u_∂, it was shown that there does indeed exist such a curve. The existence was established using sub- and super-solutions. Sub- and super-solutions to (2.2) with internal layers were then constructed and the existence of a function ϕ with the appropriate transition layer (at Γ satisfying (2.3)) was proven [**12,13**].

3. Connections to sharp interface formulations. The phase field approach differs most conspicuously from most other approaches in that (i) the interface is not sharp, and (ii) conditions at the interface are not prescribed explicitly. At a deeper level of physics, there are significant differences in that the phase field model incorporates the microscopic physics in an averaged sense. An important manifestation of this is the appearance of intrinsic length and time scales such

as correlation length, barrier or well-depth and relaxation time. In particular, a^{-1} is a measure of the well-depth in the double-well potential and is an indication of the barrier which must be crossed in the transition between phases. The interfacial thickness is of order $\sqrt{a}\xi$ while the surface tension is of order $\xi/\sqrt{a}$.

Specifically, if $G'(\phi) \equiv \phi - \phi^3$ in (1.2), (1.3), then the $O(1)$ solution to (1.3) is

$$\phi_0(r) = \tanh \frac{r}{2\sqrt{a}\xi} \tag{3.1}$$

where r is the (normal) distance from the interface, the interfacial or surface tension is

$$\sigma = \frac{2}{3}\frac{\xi}{\sqrt{a}} + o(\xi a^{-1/2}) \tag{3.2}$$

and the temperature at the interface is

$$u \cong -\frac{2}{3}\frac{\xi}{\sqrt{a}}(\kappa + \alpha v) \tag{3.3}$$

where α is defined by $\tau = \alpha\xi^2$, and v is the normal velocity (toward the liquid).

Using these relationships, one can obtain the formal result that the limit of a sharp interface can be attained in different ways depending on the scaling of ξ, α and a. The scaling of these as ξ approaches zero involves crucial assumptions about the nature of the molecular interactions of the material. At the macroscopic level they are then exhibited in (3.3) which determines the velocity of the interface based on the curvature and temperature. Thus, with appropriate scaling, one can understand the microscopic origin of various macroscopic conditions. Most significantly, with a approaching zero, the interfacial thickness can be allowed to vanish while the surface tension remains $O(1)$, leading to one of the (modified) Stefan problems in Figure 1. This differs from the limit discussed in Section 2, in which the surface tension and interfacial thickness are both $O(\xi)$. We note that these results can also be attained in anisotropic situations. In two dimensions, anisotropy may be incorporated into the model by modifying $\Delta\phi$ into $\Delta\phi + \xi_1^2\phi_{xx}$ with the result [**9**]

$$\Delta s u(r,\theta) = -[\sigma(\theta)+\sigma''(\theta)]\kappa - \frac{\tau v \sigma(\theta)}{\xi_A^2(\theta)} + \mathcal{O}(\xi^2) \tag{3.4}$$

$$\xi_A^2(\theta) \equiv \xi^2 + (\xi_1^2 - \xi^2)\cos\theta. \tag{3.5}$$

More detailed anisotropy has been considered via higher order equations [**15**] and will not be discussed here. We now formulate some sharp interface problems and consider the similarities and differences between these and the phase field equations. The classical Stefan problem can be posed as the problem of finding a function $u : [0,T] \times \Omega \to \mathbf{R}$ and a curve $\Gamma(t)$ such that

$$u_t = K\Delta u \quad \text{in } \Omega_1, \Omega_2 \tag{3.6}$$

$$l v_n = K(\nabla u_S - \nabla u_L)\cdot \hat{n} \quad \text{on } \Gamma \tag{3.7}$$

$$u = 0 \tag{3.8}$$

here Ω_1 is the liquid region defined as the set of points for which u is positive (analogously Ω_2 is the solid region with u negative) while $\Gamma(t)$ is the set of points for which $u = 0$. These equations are subject to appropriate initial (and exterior) boundary conditions for u. Thus, a key assumption in the classical Stefan model is that the phase (which we may call ϕ_S) is simply a function of u, i.e.,

$$\phi_S = \begin{cases} +1, & u > 0 \\ -1, & u < 0. \end{cases} \tag{3.9}$$

In fact, with the definition (3.9), the equations (3.6), (3.7) may be written in a weak form (Oleinik) as

$$H_t = K\Delta u, \qquad H \equiv u + \frac{l}{2}\phi_S. \tag{3.10}$$

From a physical point of view one of the main problems with the classical Stefan model is that supercooling (the presence of liquid below the freezing temperature) and superheating are excluded, contrary to physical reality. Furthermore, the condition (3.8) is an approximation which may be unrealistic for many substances, particularly if the surface tension is large. An idea which has been implemented in

an effort to remedy this problem is to replace condition (3.8) with the equilibrium condition (2.3). The model [(3.6), (3.7), (2.3)] then incorporates surface tension as a stabilizing effect [**21**] since a large surface tension and large curvature of the interface are incompatible unless the temperature is very large and negative.

A further refinement of this model is obtained by considering kinetic undercooling at the interface so that (3.8) is replaced by

$$\Delta s u(t,x) = -\sigma\kappa(t,x) - c_1\sigma v(t,x), \qquad x \in \Gamma. \tag{3.11}$$

Thus, the model [(3.6), (3.7), (3.11)] can be expected to describe the situation somewhat more accurately than the previous modification. The existence of a velocity term in (3.11) has been known to metallurgists for many years [**22**], although there has been some question about the power of v.

The phase field approach not only confirms this linear relationship, but it makes possible the calculation of the constant c_1 based on microscopic and measurable quantities. This result which was first presented in [**6**], has subsequently been derived by a formal asymptotic analysis [**8**].

It has been shown [**9**] that each of the Stefan and modified Stefan problems [(3.6), (3.7), (3.8)], [(3.6), (3.7), (2.3)] and [(3.6), (3.7), (3.11)] is a formal limit as $\xi \to 0$ of the phase field equations [(1.2), (1.3)] with the other parameters appropriately scaled. This situation is summarized by Figure 1. Note that in the steady-state case there is no distinction between equations (2.3) and (3.11). The steady-state results have been established as rigorous theorems [**12**]. In the dynamical case, some conjectures and ideas for possible theorems have been presented in [**7**].

4. Absence of strong convergence in some cases. We consider limiting cases ($\xi \to 0$) with the parameters adjusted so that one expects a particular Stefan or modified-Stefan problem in the limit. However, we would like to examine some critical situations, where unlike those presented in [**7**], one cannot expect the macroscopic situations to be similar. As a result of several examples, we would like to attain the following heuristic understanding:

(i) In a "noncritical" situation, the macroscopic behavior of [(3.6), (3.7), (3.11)] (for example) and [(1.2), (1.3)], appropriately scaled, are very similar and the difference vanishes as $\xi \to 0$.

(ii) In some "critical" situations, e.g., unstable equilibrium, there is a subtlety about the interface which is captured by the averaging of molecular interactions in the phase field equations which is not addressed by the macroscopic equations, e.g., [(3.6), (3.7), (3.11)].

In this paper we concentrate on (ii) (see [**7**] for (i)).

For concreteness, suppose we consider [(3.6), (3.7), (3.11)]. If we are given a sphere whose curvature is κ_0 and a temperature u such that

$$\Delta u = 0 \quad \text{in } \Omega_1, \Omega_2 \tag{4.1}$$

$$lv_n = K(\nabla u_S - \nabla u_L) \cdot \hat{n} = 0 \quad \text{on } \Gamma \tag{4.2}$$

$$u = -\frac{\sigma}{\Delta s}\kappa_0 \quad \text{on } \Gamma \tag{4.3}$$

then (u, Γ) will not change with time. Suppose further that $u =$ constant, with constant Dirichlet boundary conditions. If the system is perturbed in either direction, e.g., the temperature is slightly lowered momentarily, then one has

$$u < -\frac{\sigma}{\Delta s}\kappa_0 \equiv u_0. \tag{4.4}$$

Condition (3.11) asserts that the velocity must become positive in order to compensate. But a positive velocity means growth of the sphere and consequently an even smaller curvature. Hence, even the original temperature is too low and the system continues to freeze until it is entirely solid. The analogous instability occurs in the opposite direction, i.e., melting, if the temperature is raised momentarily. Note that we assume that the heat diffusion is rapid enough compared to the duration of the perturbation. We consider now some initial conditions for which the phase field equations cannot be expected to converge strongly to the sharp interface models. A most dramatic example of this is the neighborhood of the unstable equilibrium point discussed above. This is defined precisely as follows for, say, a bounded two-dimensional region Ω.

1. Choose positive constants u_0, R_0 such that

$$u_0 = -\frac{\sigma_0}{\Delta s}\frac{1}{R_0}. \tag{4.5}$$

2. For the sharp interface problem [(3.6), (3.7), (2.3)] or [(3.6), (3.7), (3.11)] choose the initial temperature to be u_0 and the interface of the solid sphere to be R_0.

3. For the phase field equations, we scale ξ, α and a so that they formally approach [(3.6), (3.7), (2.3)]. The surface tension then is exactly the value σ_0 in (4.5) (before and after the limit is attained). We now choose the initial temperature to be u_0 while the initial phase function is

$$\phi_0(r) = \tanh\left[\frac{r - R_0}{2\sqrt{a}\xi} - \xi^q\right], \qquad q > 0. \tag{4.6}$$

Note that we may also take $\phi_0(r)$ to be a function which crosses at exactly $r = R_0$ in a way that (i) $\int \phi_0^2$ is the same as in (4.6) and (ii) the derivative is not symmetric about R_0, but is larger for $r < R_0$. In this case, both the location of the interface and the surface tension are exactly the same as in the sharp interface case.

Given these initial conditions, we consider the behavior of the interface in the two cases. For the sharp interface situation the solid sphere remains unchanged. The phase field, interface, on the other hand, increases in size for all values of ξ. Whether or not it is stable

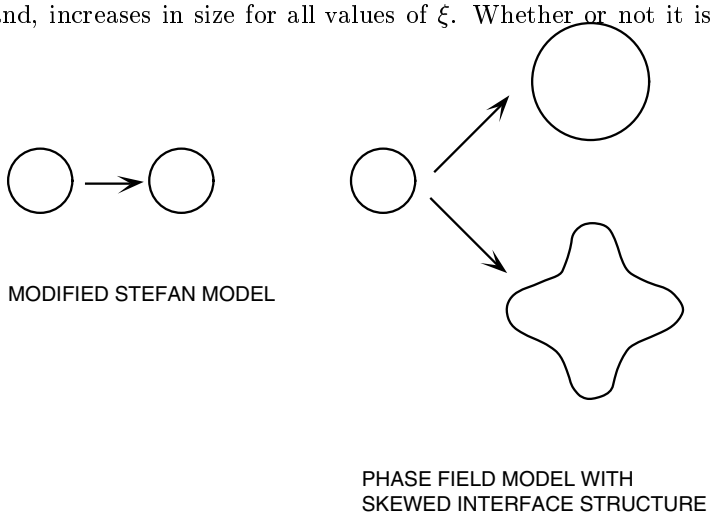

FIGURE 2. Sphere in unstable equilibrium.

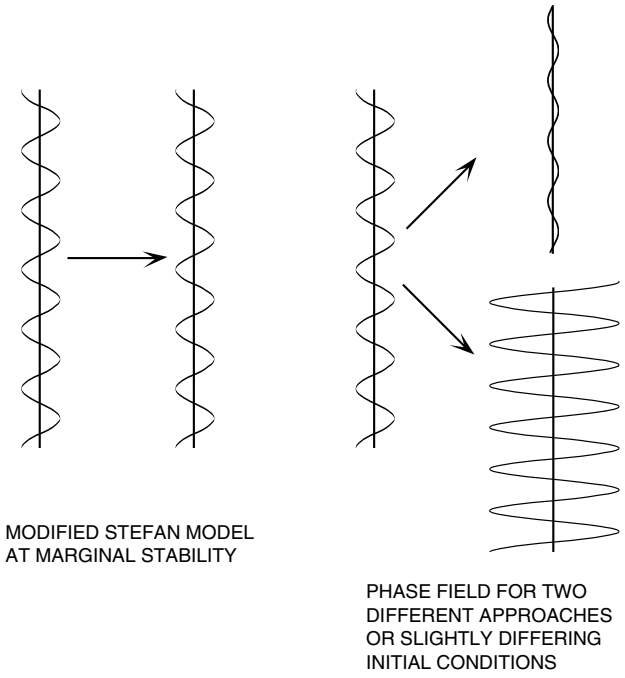

FIGURE 3. Perturbed planar front.

depends on the magnitude of the other parameters. The situation is then summarized in Figure 2.

Next, we consider a $2-d$ planar interface which is perturbed by a sine wave which has maximum curvature κ_0 corresponding to marginal stability for the plane wave with surface tension σ_0 in the model [(3.6), (3.7), (3.11)]. The precise conditions for this have been considered in [**30**]. For the phase field model we then scale ξ, a and α so that the surface tension σ_0 is approached first from above and second from below, in the manner of Section 3. Although both converge formally to [(3.6), (3.7), (3.11)], it is heuristically clear that the limit from below will be unstable while the limit from above will be stable for any nonzero value of ξ, as illustrated in Figure 3. The comments after (4.6) apply here as well.

The common feature of these two situations is that the physical problem is at an unstable equilibrium point. In the first example it is with respect to the symmetry of the sphere. In the second it is with respect to the full symmetry of $2-d$. In both examples the finer details of the interface become very significant as a result of the critical nature of the problem.

In critical situations such as these, the modified Stefan problems are not completely adequate in describing the physics of the interface since they only deal with macroscopic length scales. The second order phase field equations are one step closer to the microscopics and can distinguish between two $O(\xi)$ situations. In still more subtle situations, e.g., two sets of initial conditions which differ in $O(\xi^2)$, these equations would not necessarily be able to make the distinction at an unstable equilibrium point, for example. Such subtlety could only be depicted by the next level of physical understanding.

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