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A Microscopic Derivation of Macroscopic Sharp Interface Problems Involving Phase Transitions

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Macroscopic free boundary problems involving phase transitions (e.g., the classical Stefan problem or its modifications) are derived in a unified way from a Hamiltonian based on a general set of microscopic interactions. A Hamiltonian of the form $\mathscr{H} = \sum_{x,x'} J(x-x')\,\varphi(x)\,\varphi(x')$ leads to differential equations as a result of Fourier transforms. Expanding the Fourier transform of J in powers of q (the wave number), one can truncate the series at an *arbitrary* order M, and thereby obtain Mth-order differential equations. An asymptotic analysis of these equations in various scalings of the physical parameters then implies limits which are the standard macroscopic models for the dynamics of phase boundaries.

KEY WORDS: Interfaces; phase boundaries; Landau–Ginzburg; Stefan problem; Gibbs–Thomson effect; microscopic derivations.

1. INTRODUCTION

A question of considerable interest in nonequilibrium statistical mechanics is the derivation of macroscopic phase boundary equations from microscopic physics. A related question of justifying a mean field approach has been studied in ref. 1 for some cases. The development presented here is along the lines of previous work in which a phase or order parameter has been used to study free boundaries arising from phase transitions.[2,3] This is coupled to a heat equation with a source term which involves the order parameters. We begin by considering the (reduced) Hamiltonian on a hyperrectangular lattice $\mathscr{L}$,

$$\mathscr{H} \equiv \tfrac{1}{2} \sum_{x,x' \in \mathscr{L}} J(x-x')\,\varphi(x)\,\varphi(x') - \sum_{x \in \mathscr{L}} w(\varphi(x)) \tag{1.1}$$

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where $w(\varphi(x))$ is a double-well potential and J is the given set of interactions. Obtaining the free energy from (1.1), using Fourier transforms, and retaining terms to an arbitrary order M, one may derive the evolution equation (see refs. 4 and 5 for details),

$$\tau\varphi_t = \sum_{n=1}^{M} \varepsilon^{2n} \frac{J_{2n}}{(2n)!} (D_{11} + \cdots + D_{dd})^n \varphi - G'(\varphi) + 2au \tag{1.2}$$

where $J(x)$ is assumed (for simplicity) to be isotropic and

$$J_{2n} \equiv \int_{\mathbb{R}^d} J(x)(x_1^2 + \cdots + x_d^2)^n \, dx \tag{1.3}$$

while G is a double-well function with extrema at ± 1 and u is the temperature scaled so that $u = 0$ is the ordinary melting temperature. Alternatively, one may work with the continuum problem directly. In (1.2), τ is a (dimensionless) relaxation time and ε is a (dimensionless) length scale related to the strength of interactions. In general both of these constants are assumed to be small. The evolution equation for the phase φ is coupled to the heat equation with a source term

$$u_t + \tfrac{1}{2} l\varphi_t = K \Delta u \tag{1.4}$$

where l is the latent heat and K the diffusivity. We assume (for stability considerations) that M is odd.

In this paper we perform a detailed asymptotic analysis of [(1.2), (1.4)] and show that in various scaling limits, as τ and ε approach zero, one may attain any of the Stefan or modified Stefan models with sharp interfaces and prescribed conditions on the interface as shown in Fig. 1. A related limit, known as the quasistatic approximation in phase boundary problems, and the Hele–Shaw model in immiscible fluid flow problems, is also attained in a limit in which K approaches zero. These models may be described as follows.

A set of macroscopic equations which incorporate (i) latent heat across an interface, (ii) heat diffusion in both phases, and (iii) surface tension, curvature, and kinetic undercooling effects on the interface, can be described as follows. The problem is to determine a function $u(x, t)$ and a surface $\tilde{\Gamma}(t)$ such that

$$u_t = K \Delta u \quad \text{in} \quad \Omega \setminus \tilde{\Gamma} \tag{1.5}$$

$$lv = K(\nabla u_S - \nabla u_L) \cdot \hat{n} \quad \text{on} \quad \tilde{\Gamma} \tag{1.6}$$

$$\Delta s \, u = -\sigma\kappa - \beta\sigma v \quad \text{on} \quad \tilde{\Gamma} \tag{1.7}$$

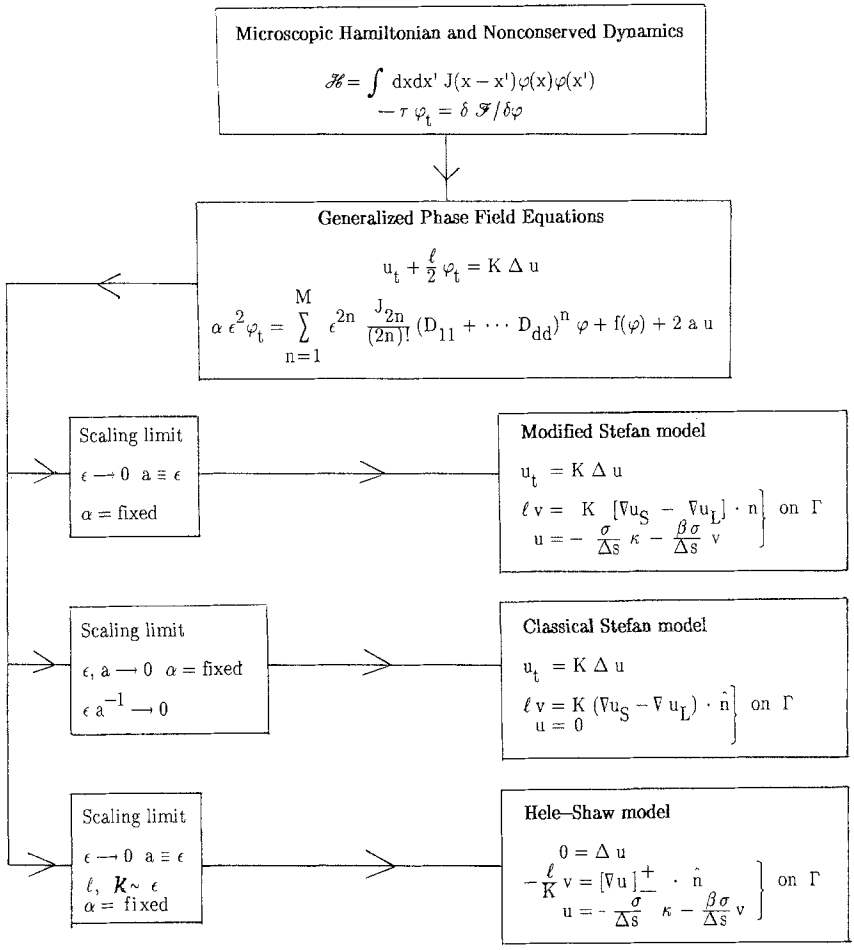

Fig. 1. The microscopic Hamiltonian and nonconserved dynamics lead to the generalized phase field equations which are Mth order differential equations as a result of truncating the Fourier series for the interactions at Mth order. By scaling the parameters in various regimes, one can obtain the standard macroscopic, or sharp interface, free boundary problems. The crucial issues in these scalings is whether various physical quantities such as the interfacial tension and kinetic undercooling coefficient vanish as the interfacial thickness approaches zero. One thus obtains models in which the interfacial behavior is drastically different.

where κ is the sum of the principal curvatures, Δs is the entropy difference between the two phases, σ is surface tension, and β is a constant which is related to a relaxation time (all constants dimensionless). The variable v is the signed (normal) velocity of Γ so that it is positive for solidification, $\hat{n}$ is the unit normal to $\tilde{\Gamma}$, and $(\nabla u_S - \nabla u_L) \cdot \hat{n}$ is the jump in the normal derivative of u across $\tilde{\Gamma}$.

If σ is set at zero, then [(1.5)–(1.7)] is called the classical Stefan model. This model does not account for any type of supercooling, since the sign of u determines the phase, unlike the modified Stefan model, i.e., [(1.5)–(1.7)] with $\sigma \neq 0$.

Another macroscopic model which has been studied is the quasistatic model, analogous to [(1.5)–(1.7)], in which (1.5) is replaced by

$$\Delta u = 0 \tag{1.8}$$

and α is generally set equal to zero. Physically this means that the heat is diffused sufficiently rapidly that the temperature profile may be regarded as being in the steady state. The set of equations [(1.6)–(1.8)] has also been used to describe the Hele–Shaw problem, i.e., the pressure between two immiscible, incompressible fluids which are between two plates.

The thrust of this work is in the uniform (formal) derivation of a broad range of macroscopic equations for sharp interface problems which arise from condensed matter physics. Furthermore, since the evolution equation (1.2) has been derived using Fourier transforms with a truncation at an *arbitrary* high order, these results establish a connection between the detailed microscopic interactions and the resulting macroscopic equations. The formal asymptotics for Eqs. (1.2), (1.4) consists of matching orders of ε in the "inner" and "outer" expansions (see Section 2) to obtain an approximation $\sum_{n=1}^{N} \varphi^{(n)}$ to the true solution φ. In principle, this procedure would become rigorous if one could prove that in some norm

$$\left\| \varphi - \sum_{n=1}^{N} \varepsilon^n \varphi^{(n)} \right\| \leqslant C(N)\, \varepsilon^N \tag{1.9}$$

An asymptotic series such as $\sum_{n=1}^{N} \varepsilon^n \varphi^{(n)}$ need not be (and usually is not) convergent in order to be useful, since the inequality (1.9) implies that one can obtain an approximation to the desired order.

These results can be generalized in a number of ways. Equation (1.4), which includes the source term $-\frac{1}{2} l \varphi_t$, is the simplest phenomenological term for an interface of finite width. The methods presented here would apply to any such source term $-l/2h(\varphi)_t$. We do not pursue a derivation of this term in this paper.

The role of microscopic anisotropy may also be readily incorporated with these methods by introducing it via $J(x)$.

2. PRELIMINARIES

Using the (reduced) Hamiltonian (1.1) and the discrete Fourier transforms[4]

$$\hat{\varphi}(q) \equiv \sum_{x \in \mathscr{L}} e^{iq \cdot x} \varphi(x), \qquad \hat{J}(q) \equiv \sum_{x \in \mathscr{L}} e^{-iq \cdot x} J(x) \tag{2.1}$$

one may write the interaction part of the Hamiltonian as

$$\sum_{x, x \in \mathscr{L}} J(x - x')\, \varphi(x)\, \varphi(x') = N^{-1} \sum_{q} \hat{J}(q)\, \hat{\varphi}(q)\, \hat{\varphi}(-q) \tag{2.2}$$

where N is the number of spins in the lattice. Upon taking the continuum limit with the procedure described in ref. 4, p. 145, one obtains the free energy

$$\mathscr{F}\{\varphi\} \equiv \int F\, dx_1 \cdots dx_d$$

$$F = \frac{1}{2a} \sum_{n=1}^{\infty} {\sum_{p_1 + \cdots p_d = 2n}}' (-1)^{n+1} \varepsilon^{2n} b(2n; p_1, \ldots, p_d) \tag{2.3}$$

$$\times (D_1^{p_1/2} \cdots D_d^{p_d/2} \varphi)^2 + \frac{1}{a} G(\varphi) - 2u\varphi$$

Here, D_i is the derivative in the ith direction and the primed sum is over all sets of positive, even numbers $\{p_1, \ldots, p_d\}$ whose sum is $2n$. The coefficients are moments of the interactions, given explicitly by

$$b(2n; p_1, \ldots, p_d) \equiv \frac{1}{p_1! \cdots p_d!} \int J(x)\, x_1^{p_1} \cdots x_d^{p_d}\, dx_1 \cdots dx_d \tag{2.4}$$

Also, a is a dimensionless length scale which determines the well depth for the double-well potential, $(1/a)\, G(\varphi)$. The convergence properties of (2.3) are contingent upon the regularity properties of φ and its derivatives.

The order parameter φ must satisfy the evolution equation $\tilde{\tau}\varphi_t = -\delta\mathscr{F}/\delta\varphi$, where $\tilde{\tau}$ is a relaxation time. If we truncate the series in (2.3) at some arbitrary integer M, then the Euler–Lagrange equations imply (in the isotropic case) the evolution equation (1.2).

The system of equations [(1.2), (1.4)] can then be studied subject to initial conditions and external boundary conditions in a region Ω in d-dimensional space. In order to discuss a single interface in a finite domain, we assume that Ω is annular (not necessarily spherically symmetric) and suppose that the inner part is solid and the outer part is liquid.

For geometries in which the interface intersects with an external container, one must incorporate the physics of three-phase (instead of two-phase) equilibrium. We denote by $\partial\Omega_-$ and $\partial\Omega_+$, respectively, the inner and outer parts of the boundary $\partial\Omega$ of Ω. We assume the boundary conditions

$$u(x, t) = u_\partial(x), \qquad x \in \partial\Omega \tag{2.5}$$

$$\varphi(x, t) = \varphi_\pm(x), \qquad \frac{\partial^j}{\partial \nu^j}\varphi(x, t) = 0, \qquad x \in \partial\Omega \quad (j = 1, \ldots, M-1) \tag{2.6}$$

where the values $\varphi_\pm$ on the outer and inner boundaries are given by the largest and smallest roots of

$$f(\varphi_\pm(x)) + 2au_\partial(x) = 0, \qquad x \in \partial\Omega \tag{2.7}$$

and ν is the normal to $\partial\Omega$. Note that for small values of a, which is of primary interest, $\varphi_\pm \approx \pm 1$. In the limit as $a \to 0$, $\varphi_\pm = \pm 1$.

Other boundary conditions can also be imposed. The results do not depend crucially on the precise nature of the external boundary conditions so long as φ is maintained at $\approx \pm 1$ near $\partial\Omega$.

The qualitative nature of the solution (u, φ) to [(1.2), (1.4)] is expected to be a transition layer behavior for φ with thickness of order ε, while the gradient of u makes a similar transition. This behavior will be confirmed by the use of matched asymptotic analysis. We let the interface be defined by

$$\Gamma(t) = \{x \in \Omega: \varphi(t, x) = 0\} \tag{2.8}$$

and let r be the normal coordinate to $\Gamma(t)$, defined so that it is positive from the solid $(\varphi < 0)$ to liquid $(\varphi > 0)$. The scaled normal derivative is defined by

$$\rho = r/\varepsilon \tag{2.9}$$

Let ψ be an approximation to the solution φ of [(1.2), (1.4)] such that for some positive constant C,

$$|\varphi - \psi| \leqslant C\varepsilon \tag{2.10}$$

The surface tension σ for this model is calculated from the free energy (2.3) to leading order using the definition

$$\sigma = \frac{1}{\text{surface area}}\left[\mathscr{F}\{\psi\} - \frac{1}{2}\mathscr{F}\{\varphi_+\} - \frac{1}{2}\mathscr{F}\{\varphi_-\}\right] \tag{2.11}$$

This surface tension has been calculated in ref. 5 [with the summation in (2.3) truncated at M] as

$$\sigma = \frac{\varepsilon}{a} \sum_{n=1}^{M} (-1)^{n+1} \frac{J_{2n}}{(2n)!} n \|\psi_n\|^2 \tag{2.12}$$

$$\psi_n \equiv \frac{\partial^n \psi}{\partial \rho^n}, \qquad \|\psi_n\|^2 \equiv \int_{-\infty}^{\infty} \psi_n^2(\rho)\, d\rho \tag{2.13}$$

Physically, the key ideas of the asymptotic analysis may be summarized as follows. The thickness of the interface is of order ε. This is evident from the form of (1.2), in which the $2n$th derivative is multiplied by ε^{2n}, thereby implying the scaling of (2.9). The surface tension, however, is of order εa^{-1}, so that the relationship between ε and a is crucial in determining the limiting surface tension as ε approaches zero. For example, a sharp interface with finite surface tension can be attained by setting $\varepsilon = a$, as discussed in Section 3.

The functions u and φ are expanded in their original variables as

$$\begin{aligned} u(x, t, \varepsilon) &= u^0(x, t) + \varepsilon u^1(x, t) + \varepsilon^2 u^2(x, t) + \cdots \\ \varphi(x, t, \varepsilon) &= \varphi^0(x, t) + \varepsilon \varphi^1(x, t) + \varepsilon^2 \varphi^2(x, t) + \cdots \end{aligned} \tag{2.14}$$

For simplicity of exposition, we assume a two-dimensional geometry and let s be a measure of arc length from some fixed point so that (r, s) is a local coordinate system. The expansions (2.13), (2.14) are called the *outer expansion*. Using the stretched variable ρ defined by (2.9), we define the *inner variables* U, ϕ by

$$\begin{aligned} u(x, t, \varepsilon) &= U(\rho, s, t, \varepsilon) = U^0(\rho, s, t) + \varepsilon U^1(\rho, s, t) + \cdots \\ \varphi(x, t, \varepsilon) &= \phi(\rho, s, t, \varepsilon) = \phi^0(\rho, s, t, \varepsilon) + \varepsilon \phi^1(\rho, s, t) + \cdots \end{aligned} \tag{2.15}$$

We use the notation that $f|_{\Gamma_\pm}$ means the limiting value of f as Γ is approached from $r > 0$ or $r < 0$, respectively. Analogous expansions are carried out for r, s, and Γ.

3. A SHARP INTERFACE LIMIT WITH FINITE SURFACE TENSION

We now perform an asymptotic analysis of the first limiting case, i.e., nonzero surface tension.

Proposition 3.1. In the formal asymptotic limit as ε approaches zero with $a \equiv \varepsilon$, $\alpha = \text{const}$, the phase field equations [(1.2), (1.4)] are

governed by the sharp interface model [(1.5)–(1.7)] with σ defined by (2.12) and $\beta \equiv \alpha \|\psi_1\|^2$. The outer expansion for u and φ in terms of the original variables is obtained by substituting (2.14) into (1.2), (1.4) and formally equating coefficients of powers of ε.

Outer Expansion

$O(1)$:

$$u_t^0 + \frac{l}{2}\varphi_t^0 = K \Delta u^0 \tag{3.1}$$

$$f(\varphi^0) = 0 \tag{3.2}$$

$O(\varepsilon)$:

$$u_t^1 + \frac{l}{2}\varphi_t^1 = K \Delta u^1 \tag{3.3}$$

$$f'(\varphi^0)\,\varphi^1 + 2u^0 = 0 \tag{3.4}$$

where $f(\varphi) \equiv -G'(\varphi)$. We note that the $O(1)$ and $O(\varepsilon)$ equations are identical for differential equations (1.2) of all orders M. One has then

$$\varphi^0 = \pm 1 \quad (\text{or } 0) \tag{3.5}$$

$$\varphi^1 = -2u^0/f'(\varphi^0) \tag{3.6}$$

Equation (3.5) thus implies that (3.1) reduces to the heat equation for all points which are not on the interface.

Inner Expansion. Using the (r, s) coordinate system, one can write the Laplacian of an arbitrary function w as

$$\Delta w = w_{rr} + \kappa w_r + |\nabla s|^2 w_{ss} + \Delta s\, w_s \tag{3.7}$$

while the time derivative w_t now becomes

$$w_t + r_t w_r + s_t w_s \tag{3.8}$$

Equations (1.4), (1.2) are then transformed by the (ρ, s) coordinate system into

$$KU_{\rho\rho} + \varepsilon\left(-r_t U_\rho - \frac{l}{2} r_t \phi_\rho + K \Delta r\, U_\rho\right)$$

$$-\varepsilon^2\left[U_t + s_t U_s + \frac{l}{2}\phi_t + \frac{l}{2} s_t \phi_s + K(|\nabla s|^2 U_{ss} + \Delta s\, U_s)\right] = 0 \tag{3.9}$$

$$\alpha\varepsilon^2(\phi_t + r_t\phi_r + s_t\phi_s)$$
$$= \sum_{n=1}^{M} \varepsilon^{2n} \frac{J_{2n}}{(2n)!}\left(\frac{\partial^2}{\partial r^2} + \kappa\frac{\partial}{\partial r} + |\nabla s|^2\frac{\partial^2}{\partial s^2} + \Delta s\frac{\partial}{\partial s}\right)^n \phi + f(\phi) + 2\varepsilon U$$
$$= \sum_{n=1}^{M} \frac{J_{2n}}{(2n)!}\left(\frac{\partial^{2n}\phi}{\partial r^{2n}} + \varepsilon n\kappa\frac{\partial^{2n-1}\phi}{\partial\rho^{2n-1}}\right) + f(\phi) + 2\varepsilon U + O(\varepsilon^2) \tag{3.10}$$

We formally equate the orders in (3.9), (3.10). Then the inner and outer solutions are "matched" using the conditions described in the Appendices of refs. 3 and 6. One has the following first-order inner problem:

$O(1)$:

$$U^0_{\rho\rho} = 0 \tag{3.11}$$

$$\sum_{n=1}^{M} \frac{J_{2n}}{(2n)!}\frac{\partial^{2n}\phi^0}{\partial r^{2n}} + f(\phi^0) = 0 \tag{3.12}$$

The general solution to (3.11) is given by

$$U^0 = c\rho + b$$

where c, b are independent of ρ. Since the matching condition

$$U^0(\pm\infty, t) = u^0(\Gamma^0_{\pm}, t) \tag{3.13}$$

cannot be satisfied unless $c = 0$, one has the first-order inner solution

$$U^0 = b \qquad \text{(independent of } \rho) \tag{3.14}$$

The boundary conditions (2.6) imposed on φ imply for the $O(1)$ inner solution the conditions

$$\phi^0(\pm\infty, t) = \pm 1, \qquad \frac{\partial^j}{\partial\nu^j}\phi^0(\pm\infty, t) = 0 \qquad (j = 1,..., M-1) \tag{3.15}$$

where the variable s has been omitted. The boundary value problem (3.12), (3.16) is an ordinary differential equation that we assume has a solution which is odd. We let $\psi(\rho)$ defined by

$$\psi \equiv \phi^0 \tag{3.16}$$

denote this solution.

The next order is given by the following:
$O(\varepsilon)$:

$$KU^1_{\rho\rho} = \frac{l}{2} r^0_t \phi^0_\rho \tag{3.17}$$

$$-\alpha v^0 \phi^0_\rho = \sum_{n=1}^{M} \frac{J_{2n}}{(2n)!} \left(\frac{\partial^{2n} \phi^1}{\partial r^{2n}} + \varepsilon n \kappa \frac{\partial^{2n-1}}{\partial \rho^{2n-1}} \phi^0 \right) + f'(\phi^0)\, \phi^1 + 2U^0 \tag{3.18}$$

where we have used (3.14) to set $U^0_\rho = 0$.

Upon integrating (3.17), one obtains

$$KU^1_\rho = \frac{l}{2} r^0_t \psi + c_1 \tag{3.19}$$

where c_1 depends on s and t, but not on ρ. Combining (3.19) with the matching condition

$$\lim_{\rho \to \pm\infty} U^1_\rho(\rho, t) = u^0_r(\Gamma^0_\pm, t) \tag{3.20}$$

one has the interface condition

$$Ku^0_r|_{\Gamma_\pm} = \pm \frac{l}{2} r^0_\pm + c_1 \tag{3.21}$$

Subtracting (3.21) with the plus sign from the minus, one has

$$K[u^0_r]^+_- = -lv^0 \tag{3.22}$$

which is the latent heat condition (1.6) to first order.

Next, consider Eq. (3.18), which we rewrite as

$$\begin{aligned} L\phi^1 &\equiv \sum_{n=1}^{M} \frac{J_{2n}}{(2n)!} \frac{\partial^{2n} \phi^1}{\partial \rho^{2n}} + f'(\phi^0)\, \phi^1 \\ &= -\varepsilon n \kappa \frac{J_{2n}}{(2n)!} \sum_{n=1}^{M} \frac{\partial^{2n-1} \psi}{\partial \rho^{2n-1}} - 2U^0 - \alpha v^0 \psi \\ &\equiv H \end{aligned} \tag{3.23}$$

Note that the homogeneous equation has ψ_ρ as a solution, i.e., $L\psi_\rho = 0$. The boundary conditions for ϕ^1 are implied by (2.6) as

$$\frac{\partial^j}{\partial v^j} \phi^1(\pm\infty, t) = 0 \qquad (j = 1, \ldots, M-1) \tag{3.24}$$

An orthogonality relation can then be obtained from the identity

$$\int_{-\infty}^{\infty} (\phi^1 L\psi_\rho - \psi_\rho L\phi^1)\, d\rho = -\int_{-\infty}^{\infty} \psi H\, d\rho \tag{3.25}$$

An application of integration by parts using (3.24) implies that the left-hand side vanishes. Rewriting the right-hand side, one obtains the relation

$$\int_{-\infty}^{\infty} \left(-\varepsilon n\kappa \frac{J_{2n}}{(2n)!} \sum_{n=1}^{M} \frac{\partial^{2n-1}\psi}{\partial\rho^{2n-1}} - 2U^0 - \alpha v^0 \psi_\rho \right) \psi_\rho\, d\rho = 0 \tag{3.26}$$

Analyzing the terms in (3.26), one obtains

$$\int_{-\infty}^{\infty} -2U^0\psi\, d\rho = -4b = -4u^0|_\Gamma \tag{3.27}$$

$$\int_{-\infty}^{\infty} -\alpha v^0 \psi_\rho^2\, d\rho = \alpha v^0 \int_{-\infty}^{\infty} \psi_\rho^2\, d\rho \tag{3.28}$$

since $U^0 = b$ is a constant and v^0 is a property of the curve on which $\rho = 0$. Also, one has, by repeated integration by parts, the identity

$$\int_{-\infty}^{\infty} \left(\frac{\partial^{2n-1}\psi}{\partial\rho^{2n-1}} \right) \left(\frac{\partial\psi}{\partial\rho} \right) d\rho = (-1)^{n-1} \int_{-\infty}^{\infty} \left(\frac{\partial^n \psi}{\partial\rho^n} \right)^2 d\rho \tag{3.29}$$

Employing the notation of (2.13), one can write

$$4u^0|_\Gamma = -\kappa \sum_{n=1}^{M} (-1)^{n+1}\, n \frac{J_{2n}}{(2n)!} \|\psi_n\|^2 - \alpha v^0 \|\psi_1\|^2 \tag{3.30}$$

Since the entropy difference[7] between phases is 4 and the surface tension is given by (2.12), one has

$$\Delta s u^0|_\Gamma = -\sigma\kappa - \alpha \|\psi_1\|^2 v^0 \tag{3.31}$$

Thus, we see that the first-order outer solution satisfies the interface relation (1.7). This is the last of the three objectives which are summarized in Proposition 3.1.

Proposition 3.2. In the formal asymptotic limit as ε and α approach zero with $a \equiv \varepsilon$, the phase field equations [(1.2), (1.4)] are governed by the sharp interface model [(1.5)–(1.7)] with $\beta \equiv 0$ and σ defined by (2.12).

The verification of this limit is similar to the previous case. The main difference is that the left-hand side of (3.18) vanishes. Consequently, the velocity term is absent in (2.31).

4. A SHARP INTERFACE LIMIT WITH ZERO SURFACE TENSION (CLASSICAL STEFAN MODEL)

The calculation of the surface tension (2.12) for the free energy which leads to (1.2) suggests that a scaling in which ε/a approaches zero leads to a sharp interface model in which surface tension vanishes. If σ is set at zero, Eqs. (1.5)–(1.7) do not incorporate surface tension. This model, which was originally introduced as a one-dimensional problem,[8] is called the classical Stefan model in the mathematics literature. The interface is known to be highly unstable in the absence of surface tension as a stabilizing factor. We present an asymptotic analysis in a scaling which is convenient for attaining this limit.

Proposition 4.1. In the formal asymptotic limit as ε approaches zero with $\varepsilon = \bar{\varepsilon}^3$, $\tau = \alpha\bar{\varepsilon}^6$ (α = fixed), and $a = \bar{\varepsilon}^2$, the phase field equations [(1.2), (1.4)] are governed by the classical Stefan model [(1.5)–(1.7), $\sigma \equiv 0$].

With this scaling, Eqs. (1.2), (1.4) can be written as

$$u_t + \frac{l}{2}\varphi_t = K\Delta u \tag{4.1}$$

$$\alpha\bar{\varepsilon}^6\varphi_t = \sum_{n=1}^{M} \bar{\varepsilon}^{6n} \frac{J_n}{(2n)!}(D_{11} + \cdots D_{dd})^n \varphi + f(\varphi) + 2\bar{\varepsilon}^2 u \tag{4.2}$$

We note that with this scaling the surface tension σ approaches zero as $\bar{\varepsilon}$ goes to zero [see (2.12)]. The asymptotic analysis is somewhat different from that of Section 3 in that the scaled variable is now

$$z = r/\bar{\varepsilon}^3 \tag{4.3}$$

Thus, the factor by which the normal variable scales is not the same as the expansion parameter $\bar{\varepsilon}$. The expansions are as follows.

Outer Expansion

$O(1)$:

$$u_t^0 + \frac{l}{2}\varphi_t^0 = K\Delta u^0 \tag{4.4}$$

$$f(\varphi^0) = 0 \tag{4.5}$$

$O(\bar{\varepsilon})$:

$$u_t^1 + \frac{l}{2}\varphi_t^1 = K\Delta u^1 \tag{4.6}$$

$$f'(\varphi^0)\,\varphi^1 = 0 \tag{4.7}$$

The $O(1)$ expansion is the same as in Section 3, so that one obtains the heat equation at all points which are not on the interface.

The inner variables are now written as

$$U(z, s, t, \bar{\varepsilon}) \equiv u(x, y, t, \bar{\varepsilon}), \qquad \phi(z, s, t, \bar{\varepsilon}) \equiv \varphi(x, y, t, \bar{\varepsilon}) \tag{4.8}$$

while Eqs. (1.2), (1.4) are transformed into

$$KU_{zz} + \bar{\varepsilon}^3 \left(-r_t U_z - \frac{l}{2} r_t \phi_z + K \Delta r \, U_z \right)$$

$$- \bar{\varepsilon}^6 \left[U_t + U_s s_t + \frac{l}{2} \phi_t + \frac{l}{2} \phi_s s_t + K(U_{ss} |\nabla s|^2 + U_s \Delta s) \right] = 0 \tag{4.9}$$

$$\sum_{n=1}^{M} \frac{J_{2n}}{(2n)!} \left(\frac{\partial^{2n} \phi}{\partial z^{2n}} + \bar{\varepsilon}^3 n\kappa \frac{\partial \phi}{\partial z} \right) + f(\phi) + 2\bar{\varepsilon}^2 U - \alpha \bar{\varepsilon}^3 r_t \phi_z + O(\bar{\varepsilon}^6) = 0 \tag{4.10}$$

The orders may now be matched formally as follows:

Inner Expansion

$O(1)$:

$$U^0_{zz} = 0 \tag{4.11}$$

$$\sum_{n=1}^{M} \frac{J_{2n}}{(2n)!} \frac{\partial^{2n} \phi^0}{\partial z^{2n}} + f(\phi^0) = 0 \tag{4.12}$$

$O(\bar{\varepsilon})$:

$$U^1_{zz} = 0 \tag{4.13}$$

$$L\phi^1 \equiv \sum_{n=1}^{M} \frac{J_{2n}}{(2n)!} \frac{\partial^{2n} \phi^1}{\partial z^{2n}} + f'(\phi^0)\, \phi^1 = 0 \tag{4.14}$$

$O(\bar{\varepsilon}^2)$:

$$U^2_{zz} = 0 \tag{4.15}$$

$$L\phi^2 \equiv \sum_{n=1}^{M} \frac{J_{2n}}{(2n)!} \frac{\partial^{2n} \phi^2}{\partial z^{2n}} + f'(\phi^0)\, \phi^2 = -\frac{1}{2} f''(\phi^0)(\phi^1)^2 - 2U^0 \tag{4.16}$$

The $O(1)$ expansion is identical to (3.11), (3.12) and results in the solutions (3.14), (3.16). Equation (4.14), subject to the boundary conditions (2.6), has the solution

$$\phi^1 = \psi' \tag{4.17}$$

Since $\psi' = \phi_z^0$ satisfies the homogeneous equation $L\psi' = 0$, the solvability condition for (4.16) implies

$$\int_{-\infty}^{\infty} \left[-\frac{1}{2} f''(\psi)(\psi')^2 - 2b \right] \psi' \, dz = 0 \tag{4.18}$$

Since f, f'' are odd and f', ψ' are even, the first term vanishes, leaving the result

$$\int_{-\infty}^{\infty} 2b\psi'(z) \, dz = 4b = 0 \tag{4.19}$$

Using the matching relation (3.13), we obtain

$$u^0|_\Gamma = 0 \tag{4.20}$$

This satisfies (1.7) with $\sigma \equiv 0$.

The latent heat condition (1.6) is the only condition which remains to be verified. Since (1.4) is identical in both forms of the phase field equations (i.e., second and higher order) and $\phi^0 = \psi$ has the same qualitative behavior, the analysis of Section 6 of ref. 3 may be used in identical form to obtain (1.6).

5. THE QUASISTATIC OR HELE–SHAW LIMIT

Proposition 5.1. In the formal asymptotic limit as ε approaches zero with $a \equiv \varepsilon$, and l, K also proportional to ε and $\alpha = \text{const}$, the phase field equations [(1.2), (1.4)] are governed by the sharp interface model [(1.6)–(1.8)] with σ defined by (2.12) and $\beta \equiv \alpha \|\psi_1\|^2$.

Remark. If α also approaches zero in Proposition 5.1, then one obtains the analog of Proposition 3.2, i.e., the velocity coefficient β is zero.

The phase field equations (1.2), (1.4) can be written as

$$\varepsilon_1 u_t + \frac{c^2}{2} \varphi_t = \Delta u \tag{5.1}$$

$$\alpha_1 \varepsilon_1^2 \varphi_t = \sum_{n=1}^{M} \varepsilon_1^{2n} \frac{J_{2n}}{(2n)!} (D_{11} + \cdots D_{dd})^n \varphi + f(\varphi) + 2\varepsilon_1 u \tag{5.2}$$

where α_1, ε_1 are α, ε rescaled by $O(1)$ constants, and $c^2 = Kl^{-1}$.

We use the procedure of Section 3 to examine the outer and inner expansions.

Outer Expansion

$O(1)$:

$$\frac{c^2}{2}\varphi_t^0 = \Delta u^0 \tag{5.3}$$

$$f(\varphi^0) = 0 \tag{5.4}$$

$O(\varepsilon_1)$:

$$u_t^0 + \frac{c^2}{2}\varphi_t^1 = \Delta u^1 \tag{5.5}$$

$$f'(\varphi^0)\,\varphi^1 + 2u^0 = 0 \tag{5.6}$$

Equations (5.4) and (5.6) are identical to (3.2) and (3.4), respectively, so that the solutions (3.5) and (3.6) are valid in this case also. Hence, Eq. (5.3) reduces to Laplace's equation (1.8) for all points which are not on the interface.

Inner Expansion

$O(1)$:

$$U_{\rho\rho}^0 = 0 \tag{5.7}$$

$$\sum_{n=1}^{M} \frac{J_{2n}}{(2n)!}\frac{\partial^{2n}\phi^0}{\partial z^{2n}} + f(\phi^0) = 0 \tag{5.8}$$

The $O(1)$ inner expansion is identical to (3.11) and (3.12), so that the solution U^0, ϕ^0 obtained in (3.14), (3.16) remains valid.

The next order is given as follows:

$O(\varepsilon)$:

$$U_{\rho\rho}^1 - \frac{c^2}{2} r_t^0 \phi_\rho^0 = 0 \tag{5.9}$$

$$-\alpha v^0 \phi_\rho^0 = \sum_{n=1}^{M} \frac{J_{2n}}{(2n)!}\left(\frac{\partial^{2n}\phi^1}{\partial z^{2n}} + \varepsilon n\kappa \frac{\partial^{2n-1}\phi^0}{\partial z^{2n-1}}\right) + f'(\phi^0)\,\phi^1 + 2U^0 \tag{5.10}$$

The analysis of the inner expansion then parallels the development of Eqs. (3.19)–(3.31), thereby verifying Proposition 5.1.

The limiting model [(1.6)–(1.8)] is a quasistatic model in the sense that temperature is always in a steady state by virtue of (1.8). These equations have also been used to describe the Hele–Shaw cell, where u is interpreted as the pressure difference between fluids.[9]

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