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The Dynamics of a Conserved Phase Field System: Stefan-like, Hele–Shaw, and Cahn–Hilliard Models as Asymptotic Limits

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The dynamics of a conserved phase field system for a free boundary, that is,

$$u_t + \tfrac{1}{2}l\varphi_t = K\,\Delta\, u,$$
$$-\tau\varphi_t = \xi^2\,\Delta\,[\xi^2\,\Delta\,\varphi + f(\varphi)/a + 2u],$$

are studied asymptotically. Many of the major macroscopic free-boundary problems arise as limits in various scalings. Temperature, curvature, surface tension, and velocity relations are derived, and compared with analogous results for systems using a nonconserved order parameter. A single fourth-order equation which has been studied in spinodal decomposition (Cahn–Hilliard) is obtained from this system of equations by setting the latent heat to zero.

1. Introduction

THE PHASE field approach to free-boundary problems has been under extensive mathematical study since 1983 [1] (see also [2, 3] and references in [4]). This approach involves the use of an 'order' parameter φ in addition to the temperature u (scaled so that $u = 0$ is the planar melting temperature). The free energy may be expressed using Landau–Ginzburg theory as

$$\mathcal{F}_u\{\varphi\} = \int \mathrm{d}^N x[\tfrac{1}{2}\xi^2(\nabla\varphi)^2 + (\varphi^2-1)^2/8a - 2u\varphi], \tag{1.1}$$

where $(\varphi^2-1)^2/8a$ is a prototype double-well potential (which may be generalized to an $F(\varphi)$ having similar qualitative properties, i.e. symmetric double-well potential with minima at ± 1). The significance of ξ and a is discussed in [4]. The heat balance is given by

$$u_t + \tfrac{1}{2}l\varphi_t = K\,\Delta\, u, \tag{1.2}$$

where l and K are constants. The thrust of this approach to nonequilibrium problems is in stipulating that (1.2) is coupled to an evolution equation

$$\tau\varphi_t = -\frac{\delta\mathcal{F}}{\delta\varphi}, \tag{1.3}$$

where τ is a relaxation time. Equation (1.3) can be written as

$$\tau\varphi_t = \xi^2\,\Delta\,\varphi + (\varphi-\varphi^3)/2a + 2u, \tag{1.4}$$

so that (1.2),(1.4), subject to initial and boundary conditions, form a parabolic system for (u, φ) which has a unique smooth solution [1].

In condensed-matter physics, an order parameter is a macroscopically observable property (e.g. mechanical, magnetic, etc.) which can be traced, like most macroscopic quantities, to a statistical mechanical average and which serves to distinguish one phase from another [5: p. 3]. Typical examples of order parameters are zero-field magnetization or density. It is well known that order parameters for some systems are conserved quantities, while others are nonconserved [5]. The differences have been explored in the context of critical phenomena in equilibrium problems. In this paper, we analyse in detail the model proposed in [6] involving the conserved analogue of (1.2),(1.4). The model is based on Cahn–Hilliard type ideas for an interface [11, 22, 16]. In particular, the evolution equation (1.3) is replaced by the corresponding equation (see [18] for derivation)

$$-\tau\varphi_t = \xi^2 \Delta\left(\frac{\delta \mathcal{F}}{\delta\varphi}\right). \tag{1.5}$$

The new system then consists of (1.2) coupled with

$$-\tau\varphi_t = \xi^2 \Delta\,[\xi^2 \Delta\, \varphi + f(\varphi)/a + 2u] \tag{1.6}$$

(where $f \equiv F'$), subject to initial and boundary conditions on a domain $\Omega \subset \mathbb{R}^d$. The interface $\Gamma(t)$, is defined as the set of points for which $\varphi(x, t) = 0$. All parameters in (1.2),(1.6) are dimensionless (see [1] for physical interpretation). In some of the limits we consider, ξ and a (and in some cases τ) will be small parameters.

The main results of the paper are as follows.

(i) We show that all of the major Stefan-like and Hele–Shaw (or quasi-static) type models arise from (1.2),(1.6) as a consequence of formal matched asymptotic analysis.

(ii) We determine the interfacial condition relating temperature, curvature, surface tension, velocity, and relaxation time (see (5.6) and (9.2)), in a way similar to those studied in [3, 19, 7, 8] for nonconserved systems. A single equation of the type (1.4) with $u = 0$ was used previously [17] to obtain a velocity–curvature relation.

(iii) We obtain an understanding of the limit in which one has just the fourth-order equation [12]

$$-\tau\varphi_t = \xi^2 \Delta\,[\xi^2 \Delta\ + f(\varphi)/a]. \tag{1.7}$$

This is the Cahn–Hilliard spinodal decomposition limit in which the latent heat vanishes.

(iv) The most important practical implication of this study is that it provides a framework for approximating a sharp interface problem with a smooth diffuse interface in which the parameter is a locally conserved quantity. If one is interested in obtaining numerical results for any of the Stefan or Hele–Shaw models, or their modifications, then one can do the computations on equations (1.2),(1.6) with the parameters adjusted in accordance with the discussions of

Sections 4–7. The boundary conditions imposed on (1.2),(1.6) must be consistent with those desired on the sharp interface problem. For example, the boundary conditions (3.10),(3.11) lead to Neumann conditions on the temperature. An analogous limiting procedure is available for Dirichlet conditions. These results provide the conserved order parameter counterpart to results obtained in [8].

An informative recent discussion of both conserved and nonconserved Landau–Ginzburg type models may be found in [18], where the motivation for (1.5) is discussed.

After completion of this paper, we received a preprint [22] in which (1.7) alone is considered asymptotically.

2. Some basic physical concepts

A preliminary observation is that the free energy $\mathcal{F}$ is identical in the conserved and nonconserved systems. In particular, this means that many of the local equilibrium properties of the interface should be identical. The calculation of the surface tension σ is once again (see [1: Theorem 7.3] and [7: (3.10)])

$$\sigma = \frac{\epsilon}{a}\int_{-\infty}^{\infty} \psi_\rho^2 \, \mathrm{d}\rho, \tag{2.1}$$

where $\epsilon^2 = \xi^2 a$ and ψ is the (unique) solution to

$$\psi'' + f(\psi) = 0, \qquad \psi(\pm\infty) = \pm 1, \qquad \psi(0) = 0. \tag{2.2}$$

The entropy density difference between liquid and solid, Δs, is again $4 + O(\epsilon)$, as shown in [1: (7.31)].

Furthermore, since the Gibbs–Thomson relation at the interface, that is,

$$u = -\frac{\sigma}{\Delta s}\kappa, \tag{2.3}$$

where κ is the (local) sum of principal curvatures, is an equilibrium property, one expects that (2.3) is necessarily satisfied by any solution to the equilibrium problem (see Section 9).

3. Preliminaries for asymptotics

We use the notation of [7, 8] and develop an inner and outer expansion for u and φ in (1.2),(1.6). In a small neighbourhood of $\Gamma(t)$, we define $r(x, y, t)$ to be the $\pm$ distance from (x, y) to $\Gamma(t)$ such that the positive (resp. negative) sign is in the direction of positive (resp. negative) φ. We assume that the interface $\Gamma(t)$ will be regular if the initial and boundary conditions are sufficiently smooth. Similarly, $s(x, y, t)$ is defined as an arc length from a fixed point so that (r, s) is a local (moving) coordinate system. We expand the variables u, φ, r, s on the original coordinates (for some parameter ϵ to be defined) as

$$u(x, y, t, \epsilon) = u^0(x, y, t) + \epsilon u^1(x, y, t) + \epsilon^2 \cdots \tag{3.1}$$

and similarly for the other variables. The terms on the right-hand side are required to be smooth for $r \neq 0$ but may be discontinuous at $r = 0$.

The inner expansion is defined in terms of the 'stretched variable'

$$\rho = r/\delta, \tag{3.2}$$

where δ will usually be equal to ϵ, but in some cases will be some power of ϵ (as in Section 6). The inner expansion consists of writing

$$U(\rho, s, t, \epsilon) \equiv u(x, y, t, \epsilon) = U^0(\rho, s, t) + \epsilon U^1(\rho, s, t) + \epsilon^2 \cdots, \tag{3.3}$$

$$\phi(\rho, s, t, \epsilon) \equiv \varphi(x, y, t, \epsilon) = \phi^0(\rho, s, t) + \epsilon\phi^1(\rho, s, t) + \epsilon^2 \cdots. \tag{3.4}$$

We use the notation

$$f|_{\Gamma_+} \equiv \lim_{r \to 0+} f(r, s, t) \tag{3.5}$$

and analogously for Γ_-, while the jump in a function f across the interface will be defined as

$$[f]_-^+ = \lim_{r \to 0+} f - \lim_{r \to 0-} f. \tag{3.6}$$

The dependence on s will be omitted when s does not play a role.

A key aspect of the asymptotics is the matching of inner and outer solutions defined above by a well-known procedure. These may be written as (see [7] for $\delta = \epsilon$ and [8] for $\delta = \epsilon^k$ $(k \geq 2)$)

$$\lim_{\rho \to \pm\infty} U^0(\rho, t) = u^0(\Gamma^0_\pm, t) \quad (k \geq 1), \tag{3.7}$$

$$\lim_{\rho \to \pm\infty} \left(\frac{U^1(\rho, t) - \{u^1(Y^0_\pm(t), t) + [\rho + Y^1(t)]u^0_r(Y^0_\pm(t), t)\}}{\rho} \right) = 0 \quad (k = 1), \tag{3.8}$$

$$\lim_{\rho \to \pm\infty} U^1(\rho, t) = u^0_r(Y^0_\pm(t), t)Y^1_\pm(t) + u^1(Y^0_\pm(t), t) \quad (k \geq 2), \tag{3.9}$$

and similarly for φ. We write Y in place of Γ to indicate that the conditions above are one dimensional which is all that is necessary.

Although the asymptotics can be applied to any reasonable domain, we assume for simplicity of discussion that Ω is a smooth annular domain (not necessarily spherically symmetric), in which the inner part $\partial\Omega_-$ of the boundary is on the solid side, while the outer part $\partial\Omega_+$ is on the liquid side. We impose the boundary conditions

$$\frac{\partial u}{\partial v}(t, x) = 0 \quad (x \in \partial_\pm\Omega, \text{ all } t), \tag{3.10}$$

$$f(\varphi_\pm(x, t)) + 2au_{\partial_\pm}(x) = 0 \quad (x \in \partial_\pm\Omega, \text{ all } t), \tag{3.11}$$

where φ_+ is the largest root of (3.11) (and is close to $+1$ if a is small), and φ_- is the smallest root (and is close to -1 if a is small). In addition to (3.10),(3.11), we impose

$$\frac{\partial \varphi}{\partial v}(x, t) = 0 \quad (x \in \partial\Omega, \text{ all } t). \tag{3.12}$$

One can also replace (3.10),(3.12) by taking Dirichlet conditions on u and assuming that the normal derivative of the left-hand side of (3.11) vanishes. Initial conditions can be assumed to be of the form

$$u(x,0)=u_0(x), \quad \varphi(x,0)=\varphi_0(x) \quad (x\in\Omega). \tag{3.13}$$

The boundary conditions (3.11) ensure that φ is approximately ±1 on the exterior boundaries (for small a). Equation (3.11) can be modified considerably, so long as a is small and $\varphi\approx\pm1$ on the external boundaries. The analysis is similar but more lengthy. Equation (3.12) ensures that φ is level (no transition layer) at the external boundaries. Note that the order parameter is not conserved 'globally' under these boundary conditions. This is analogous to studying the heat equation (in which temperature is conserved) under Dirichlet boundary conditions, such as (3.10), which allow heat to enter or leave the system.

If one is using the equations (1.2),(1.6) as a means of approximating any of the sharp interface problems discussed in Sections 4–7, then the boundary conditions may be chosen with respect to the desired limit. In particular, if one chooses to approximate, for example, the classical Stefan problem (Section 6), subject to Neumann boundary conditions (on the temperature, u), then one uses (3.10),(3.11). As shown in Section 6, the limit consists of $\varphi=\pm1$, leaving (3.10) as the only boundary condition. The limiting physical problem, then, would be an ice–water mixture in a thermos.

The notation Ω_+ will denote the portion of $\Omega\backslash\Gamma$ which lies on the $r>0$ side of Γ, and similarly for Ω_-. Also, Ω_+ has boundary $\partial\Omega_+=\partial_+\Omega\oplus\Gamma$. We note that the geometry chosen here is simply to avoid the issue of the intersection of the interface $\Gamma(t)$ with the external boundary $\partial\Omega$. A meaningful discussion of this issue would require the incorporation of the physics of a three-phase equilibrium (where the wall is regarded as a separate phase).

Using the moving local coordinate system (r,s) one has, for any function w,

$$\Delta w\to w_{rr}+\kappa w_r+|\nabla s|^2 w_{ss}+\Delta s w_s, \tag{3.14}$$

$$w_t\to w_t+r_t w_r+s_t w_s. \tag{3.15}$$

With $\rho=r/\epsilon$ and $\epsilon\equiv a\equiv\xi^2$, equations (1.2) and (1.6) can be written as

$$KU_{\rho\rho}+\epsilon(-r_tU_\rho-\tfrac{1}{2}lr_t\phi_\rho+K\kappa U_\rho)$$
$$-\epsilon^2[U_t+s_tU_s+\tfrac{1}{2}l\phi_t+\tfrac{1}{2}ls_t\phi_s+K(|\nabla s|^2U_{ss}+\Delta sU_s)]=0, \tag{3.16}$$

$$-\tau\epsilon^2\Big(\frac{1}{\epsilon}r_t\phi_\rho+\phi_t+s_t\phi_s\Big)$$
$$=\frac{\partial^2}{\partial\rho^2}[\phi_{\rho\rho}+f(\phi)]+\epsilon\Big(\frac{\partial^2}{\rho^2}(\kappa\phi_\rho+2u)+\kappa\frac{\partial}{\partial\rho}[\phi_{\rho\rho}+f(\phi)]\Big)$$
$$+\epsilon^2\Big(|\nabla s|^2\frac{\partial^2}{\partial s^2}+\Delta s\frac{\partial}{\partial s}\Big)[\phi_{\rho\rho}+f(\phi)+\epsilon\kappa\phi_\rho+2\epsilon U+\epsilon^2(|\nabla s|^2\phi_{ss}+\Delta s\phi_s)], \tag{3.17}$$

and analogously when $\rho=r/\epsilon^k$ as in Section 6.

We note that for any nonzero ε there is some subtlety in determining the precise interfacial region. This issue has been resolved in [1].

4. The alternative modified Stefan limit

We consider (1.2),(1.6) with the parameters scaled, so that $\xi a^{-\frac{1}{2}} =$ fixed and $\tau = o(1)$. For concreteness, we suppose

$$\epsilon \equiv a = \xi^2, \qquad \tau = \epsilon, \qquad \delta \equiv \epsilon, \tag{4.1}$$

so that $\rho = r/\epsilon$ in (3.2). The equations (1.2),(1.6) then become

$$u_t + \tfrac{1}{2} l \varphi_t = K \,\Delta\, u, \tag{4.2}$$

$$-\epsilon^3 \varphi_t = \epsilon^2 \Delta \,[\epsilon^2 \Delta\, \varphi + f(\varphi) + 2\epsilon u]. \tag{4.3}$$

By formally equating powers in ϵ we obtain, for $r \neq 0$, the following.

The Outer Expansion

$O(1)$:

$$u_t^0 + \tfrac{1}{2} l \varphi_t^0 = K \,\Delta\, u^0, \tag{4.4}$$

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

Clearly, $\varphi^0 = \pm 1$ are solutions to (4.5). We show that $\varphi^0 = +1$ is the unique solution in the liquid region (i.e. $r > 0$). For any fixed t, let

$$w(x) \equiv f\big(\varphi^0(x, t)\big) \quad (x \in \Omega). \tag{4.6}$$

Then, w satisfies, by (4.5) and (3.11),(3.12), the problem

$$\begin{aligned} &\Delta w = 0 \quad \text{in } \Omega_+, \\ &w = 0, \quad \frac{\partial w}{\partial \nu} = 0 \qquad \text{on } \partial_+ \Omega. \end{aligned} \tag{4.7}$$

Since $\partial_+ \Omega$ contains an open smooth portion of $\partial \Omega_+$, one must have $w = 0$ on all of Ω_+ [9: p. 27]. Hence, $f(\varphi^0) = 0$ in Ω_+ and likewise in Ω_-. Since φ^0 is $+1$ on $\partial_+ \Omega$ and is -1 on $\partial_- \Omega$, we must conclude

$$\varphi^0(x, t) = +1 \quad (x \in \Omega_+, \text{ all } t), \qquad \varphi^0(x, t) = -1 \quad (x \in \Omega_-, \text{ all } t). \tag{4.8}$$

Using (4.8) in (4.4), we see immediately that

$$u_t^0 = K \,\Delta\, u^0 \quad (x \in \Omega \backslash \Gamma, \text{ all } t), \tag{4.9}$$

so that the heat equation is obtained as the first-order outer problem. This is the first of three main objectives.

$O(\epsilon)$:

$$u_t^1 + \tfrac{1}{2} l \varphi_t^1 = K \,\Delta\, u^1, \tag{4.10}$$

$$-\varphi_t^0 = \Delta[f'(\varphi^0)\varphi^1 + 2u^0]. \tag{4.11}$$

Note that the left-hand side of (4.11) vanishes by (4.8). Furthermore, one has

$$f'(\varphi^0)\varphi^1 + 2u^0 = 0 \quad (x \in \partial_+ \Omega \cup \partial_- \Omega, \text{ all } t), \tag{4.12}$$

since it is just the $O(\epsilon)$ part of (3.11). Hence, the argument which leads to (4.8) now implies, using the boundary conditions at the $O(\epsilon)$ level,

$$\varphi^1 = -2u^0/f'(\varphi^0), \tag{4.13}$$

so that (4.10) can be written as

$$u_t^1 - K \,\Delta\, u^1 = l u_t^0 / f'(\varphi^0). \tag{4.14}$$

The Inner Expansion

With the scaling of τ given by (4.1) one has

$O(1)$:
$$U^0_{\rho\rho}=0, \tag{4.15}$$
$$\frac{\partial^2}{\partial\rho^2}[\phi^0_{\rho\rho}+f(\phi^0)]=0. \tag{4.16}$$
$O(\epsilon)$:
$$KU^1_{\rho\rho}=\tfrac{1}{2}lr^0_t\phi^0_\rho, \tag{4.17}$$
$$0=\frac{\partial^2}{\partial\rho^2}\left(\frac{\partial^2\phi^1}{\partial\rho^2}+f'(\phi^0)\phi^1+\kappa^0\phi^0_\rho+2U^0\right). \tag{4.18}$$

Note that $\kappa^0[\phi^0_{\rho\rho}+f(\phi^0)]$ has been omitted from (4.18) since it vanishes as a consequence of (4.22).

Equation (4.15) has solutions $U^0=a\rho+b$. The matching condition (3.7) applies, so that $a=0$. Otherwise, u^0 would be unbounded at $\Gamma_\pm$. Hence, one has

$$U^0=b \quad (b \text{ independent of } \rho). \tag{4.19}$$

Integrating (4.16), $\int_{-\infty}^{\rho}\mathrm{d}\bar\rho$, one obtains

$$\frac{\partial}{\partial\rho}[\phi^0_{\rho\rho}+f(\phi^0)]\Big|_{\bar\rho=-\infty}^{\bar\rho=\rho}=0. \tag{4.20}$$

The first matching condition (3.7) applied to ϕ^0 implies that $f(\phi^0)$ vanishes at $\rho=-\infty$ and that ϕ^0 is independent of ρ for large values of $|\rho|$. Hence, the $\bar\rho=-\infty$ part of (4.20) vanishes, and we obtain

$$\frac{\partial}{\partial\rho}[\phi^0_{\rho\rho}+f(\phi^0)](\rho)=0. \tag{4.21}$$

Repeating this integration on (4.21), one has

$$\phi^0_{\rho\rho}+f(\phi^0)=0. \tag{4.22}$$

From the definition of Γ (just after equation (1.6)), one has $\phi(0,s,t)=0$, so that $\phi^0(0,s,t)=0$. Using the first matching condition (3.7) on ϕ, along with (4.8), one concludes that $\phi^0=\psi$, where ψ is the (unique) solution of

$$\psi''+f(\psi)=0, \tag{4.23}$$
$$\psi(0)=0, \qquad \psi(\pm\infty)=\pm1. \tag{4.24}$$

Hence, the $O(\epsilon)$ inner problem is solved except for the constant b in (4.19). This will be evaluated, as a consequence of a solvability condition at the $O(\epsilon)$ level.

In order to analyse (4.18), we first remark on the boundary conditions for the terms enclosed in parentheses in (4.18) at $\rho=-\infty$. Since (3.7) implies ϕ^0_ρ and $\phi^0_{\rho\rho}$ vanish at $\rho=-\infty$, we consider the remaining terms $f'(\phi^0)\phi^1+2U^0$. Using the second matching condition (3.8) on ϕ^1 and noting that $\phi^0_r=0$ $(r\neq 0)$ by (4.8), one has

$$\lim_{\rho\to\pm\infty}\phi^1(\rho,t)=\varphi^1(\Gamma_\pm(t),t). \tag{4.25}$$

Combining (4.25) with the first matching condition applied to U^0, one may write

$$\lim_{\rho\to-\infty} f'(\phi^0)\phi^1 + 2U^0 = f'(\varphi^0)\varphi^1 + 2u^0|_{\Gamma_-} = 0, \tag{4.26}$$

where the second identity follows from (4.13).

Using this boundary condition at $-\infty$, one can now integrate (4.18) twice ($\int_{-\infty}^{\rho} \mathrm{d}\bar{\rho}$) to obtain

$$L\phi^1 \equiv \frac{\partial^2}{\partial\rho^2}\phi^1 + f'(\phi^0)\phi^1 = -2U^0 - \kappa^0\phi^0_\rho + O(\epsilon^2) \equiv G. \tag{4.27}$$

Noting that ϕ^0_ρ solves the homogeneous equation, $L\phi^0_\rho = 0$, corresponding to (4.27), one may use a Fredholm alternative theorem to imply that the L^2 inner product (ϕ^0_ρ, G) vanishes. Using the fact that U^0 is constant (see (4.19)), one has

$$4U^0 = 4u^0|_{\Gamma_\pm} = -\sigma\kappa^0, \tag{4.28}$$

$$\sigma \equiv \int_{-\infty}^{\infty} (\psi')^2\,\mathrm{d}\rho, \tag{4.29}$$

where σ is the $O(1)$ term in the surface tension (see (2.1)). Hence, we have attained the second of three main objectives.

Finally, we analyse (4.17) and show that this implies the latent heat condition. Integrating (4.17), one has, with c_1 depending on s and t but not on r,

$$KU^1_\rho = \tfrac{1}{2} l r^0_t \psi + c_1. \tag{4.30}$$

The second matching condition, (3.8), implies

$$\lim_{\rho\to\pm\infty} U^1_\rho(\rho, t) = u^0_r(\Gamma^0_\pm, t). \tag{4.31}$$

Using (4.31) in (4.30) and subtracting the Γ^0_- limit from the Γ^0_+ limit, one obtains, as in [7],

$$K[u^0_r]^+_- = -lv^0, \tag{4.32}$$

where $v^0 = -r^0_t$.

One may sum up the main conclusions with the following proposition.

PROPOSITION 4.1 *In the limit as ξ and τ approach zero with $\xi a^{-\frac{1}{2}}$ fixed, there exist asymptotic solutions to the conserved phase field equations* (1.2), (1.6), (3.10)–(3.13) *which have internal layers and are governed, in a formal asymptotic sense, by*

$$u_t = K\,\Delta u \quad \text{in } \Omega_\pm, \tag{4.33}$$

$$-lv = K[\nabla u \cdot \hat{n}]^+_- \quad \text{on } \Gamma, \tag{4.34}$$

$$u = -(\sigma/\Delta s)\kappa \quad \text{on } \Gamma, \tag{4.35}$$

where $\hat{n}$ is the unit normal to Γ.

5. The modified Stefan limit

We consider equations (1.2),(1.6) with parameters scaled so that

$$\varepsilon \equiv a = \xi^2, \qquad \tau = O(1), \qquad \delta \equiv \epsilon \text{ in (3.2)}. \tag{5.1}$$

This will result in the limit in which dynamical undercooling and curvature are both taken into account. Then equations (1.2),(1.6) are rewritten as

$$u + \tfrac{1}{2} l \varphi_t = K \Delta u, \tag{5.2}$$

$$-\tau \epsilon^2 \varphi_t = \epsilon^2 \Delta [\epsilon^2 \Delta \varphi + f(\varphi) + 2\epsilon u]. \tag{5.3}$$

PROPOSITION 5.1 *In the limit as ξ approaches zero with $\xi a^{-\frac{1}{2}}$ and τ fixed, there exist asymptotic solutions to the conserved phase field equations* (1.2), (1.6), (3.10)–(3.13) *which have internal layers and are governed, in a formal asymptotic sense, by*

$$u_t = K \Delta u \quad in\ \Omega_\pm, \tag{5.4}$$

$$-lv = K[\nabla u]_-^+ \quad on\ \Gamma, \tag{5.5}$$

$$u = -(\sigma/\Delta s)\kappa + (\tau c_0/\Delta s)v \quad on\ \Gamma, \tag{5.6}$$

where

$$c_0 \equiv \int_{-\infty}^{\infty} \psi'(\rho) \int_{-\infty}^{\rho} [\psi(\bar{\rho}) + 1]\, d\bar{\rho}\, d\rho. \tag{5.7}$$

This limit is verified using the same methods as in Section 4. The main differences are that (4.5) becomes

$$-\tau \varphi_t^0 = \Delta f(\varphi^0) \tag{5.8}$$

and $-\tau r_t^0 \phi_\rho^0$ must be added to the left-hand side of (4.18). The latter results in the velocity contribution to (5.6).

Note that, while $\varphi^0 = \pm 1$ solves the $O(1)$ outer problem as in (4.5), in this case, one cannot exclude the possibility of other nontrivial solutions.

The velocity contribution in (5.6) differs in sign and magnitude from the nonconserved case. The reason is that the boundary conditions provide a source of the '+1 phase' on the outer boundary and a sink for the '−1 phase' on the inner boundary. One may consider, for example, a mixture of A atoms and B atoms, so that '+1 phase' is A-rich while the '−1 phase' is B-rich. The boundary conditions then allow the addition and subtraction of the A and B molecules. This is analogous to the grand canonical partition function in statistical mechanics. Note that, if one used conserved boundary conditions, as in [14], that is,

$$\frac{\partial}{\partial v}[\xi^2 \Delta \varphi + f(\varphi)/a + 2u] = 0 \quad \text{on } \partial\Omega, \tag{5.9}$$

then an established single interface would not move. Otherwise, global conservation would be violated.

6. The classical Stefan limit

The classical Stefan limit is attained by allowing both the surface tension and interfacial thickness to approach zero simultaneously. This differs from the previous two limits in which interfacial thickness approached zero while the surface tension remained fixed. The ideas of Section 2 then suggest the following proposition.

PROPOSITION 6.1 *In the limit as ξ, τ, a, and $\xi a^{-\frac{1}{2}}$ approach zero, there exist asymptotic solutions to the conserved phase field equations* (1.2), (1.6), (3.10)–(3.13) *which have internal layers and are governed, in a formal asymptotic sense, by*

$$u_t = K\,\Delta u \quad \text{in } \Omega_\pm, \tag{6.1}$$

$$-lv = K[\bar{\nabla} u \cdot \hat{n}]_-^+ \quad \text{on } \Gamma, \tag{6.2}$$

$$u = 0 \quad \text{on } \Gamma. \tag{6.3}$$

Note that there is more flexibility in the scaling of ξ and a, compared to Section 4. We verify this in the scaling regime defined by

$$\xi^2 \equiv a = \xi, \qquad \tau \equiv \alpha\epsilon^4 \quad (\text{where } \alpha = \text{fixed}). \tag{6.4}$$

Since the interfacial thickness is expected to be of order ϵ^3 in this case, we define $\delta = \epsilon^3$, so that the inner variable now becomes

$$\rho = r/\epsilon^3. \tag{6.5}$$

In terms of ϵ, equations (1.2),(1.6) can be written as

$$u_t + \tfrac{1}{2} l\varphi_t = K\,\Delta u, \tag{6.6}$$

$$-\alpha\epsilon^2\varphi_t = \Delta[\epsilon^6\,\Delta\,\varphi + f(\varphi) + 2\epsilon^2 u]. \tag{6.7}$$

The boundary condition (3.11) now has $a = \epsilon^2$ with this scaling. One has the following.

The Outer Expansion (for $r \neq 0$)

$O(1)$:

$$u_t^0 + \tfrac{1}{2} l\varphi_t^0 = K\,\Delta u^0, \tag{6.8}$$

$$\Delta f(\varphi^0) = 0. \tag{6.9}$$

$O(\epsilon)$:

$$u_t^1 + \tfrac{1}{2} l\varphi_t^1 = K\,\Delta u^1, \tag{6.10}$$

$$\Delta[f'(\varphi^0)\varphi^1] = 0. \tag{6.11}$$

The outer expansion is identical to that of Section 4 (note that $\varphi_t^0 = 0$ in (4.11)). In particular, $\varphi^0 = \pm 1$ in $\Omega_\pm$ so that the heat equation is obtained in Ω_1 as a result of (6.8).

The boundary conditions (3.11) can be written (in the outer expansion) as

$$0 = f(\varphi^0) + \epsilon f'(\varphi^0)\varphi^1 + \epsilon^2[f'(\varphi^0)\varphi^2 + f''(\varphi^0)(\tfrac{1}{2}\varphi^1)^2 + 2u^0]|_{\partial\Omega} + O(\epsilon^3).$$

Hence one has $\varphi^1|_{\partial\Omega} = 0$ in this case.

Since $f'(\phi^0) = \text{constant}$, (6.11) implies $\Delta\varphi^1 = 0$. Using the argument which led to (4.8), one sees that φ^1 vanishes in Ω.

The inner expansion is quite different since the stretched variable ρ is now stretched differently and the second matching condition [8] is given by (3.9). With

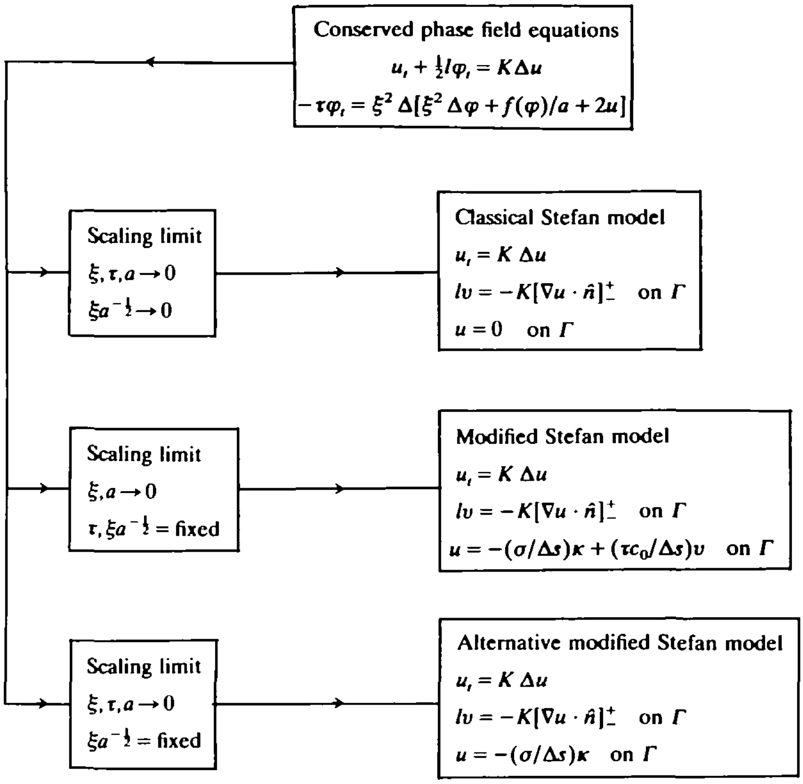

FIG. 1. Stefan-type models as limiting cases of the conserved phase field equations.

the scaling (6.4), equations (1.2),(1.6) are written as

$$KU_{\rho\rho} + \epsilon^3(-r_t U_\rho - \tfrac{1}{2}lr_t\phi_\rho + K\kappa U_\rho) - \epsilon^6[U_t + U_s s_t + \tfrac{1}{2}l\phi_t + \tfrac{1}{2}l\phi_s s_t + K(|\nabla s|^2 U_{ss} + \Delta s U_s)] = 0, \tag{6.12}$$

$$\left.\begin{aligned} -\alpha\epsilon^8\left(\phi_t + r_t\frac{1}{\epsilon}\phi_\rho + s_t\phi_s\right) &= \frac{\partial^2}{\partial\rho^2}B + \epsilon^3\kappa\frac{\partial}{\partial\rho}B + \epsilon^6\left(|\nabla s|^2\frac{\partial^2}{\partial s^2} + \Delta s\frac{\partial}{\partial s}\right)B, \\ B &= \phi_{\rho\rho} + \epsilon^3\kappa\phi_\rho + \epsilon^6|\nabla s|^2\phi_{ss} + \epsilon^6\phi_s + 2\epsilon^2 U + f(\varphi). \end{aligned}\right\} \tag{6.13}$$

One has, from (6.12) and (6.13), the following.

The Inner Expansion

$O(1)$:
$$U^0_{\rho\rho} = 0, \tag{6.14}$$

$$\frac{\partial^2}{\partial\rho^2}[\phi^0_{\rho\rho} + f(\phi^0)] = 0. \tag{6.15}$$

Since the $O(1)$ outer expansion and the first matching condition (3.7) remain the same as in Section 4, one again has $\phi^0 = \psi$ (defined by (4.23),(4.24)). The fact that $U^0 = b$ (independent of ρ) also follows for the same reason. Using the fact that ϕ^0 satisfies (4.23), the next orders can be written as

$O(\epsilon)$:
$$U^1_{\rho\rho}=0, \tag{6.16}$$
$$\frac{\partial^2}{\partial\rho^2}[\phi^1_{\rho\rho}+f'(\phi^0)\phi^1]=0. \tag{6.17}$$

$O(\epsilon)$:
$$U^2_{\rho\rho}=0, \tag{6.18}$$
$$\frac{\partial^2}{\partial\rho^2}[\phi^2_{\rho\rho}+f'(\phi^0)\phi^2+2U^0+f''(\phi^0)(\tfrac{1}{2}\phi^1)^2]=0. \tag{6.19}$$

The interface temperature (6.3) can be extracted from (6.17),(6.18). Noting that the comments of Section 4 on the boundary conditions at $\rho=-\infty$ for (6.17) still apply, one has

$$L\phi^1\equiv\phi^1_{\rho\rho}+f'(\phi^0)\phi^1=0. \tag{6.20}$$

Recalling that $\varphi^1=0$ and $\varphi^0_r=0$ in the outer expansion, while the second matching condition (3.9) implies

$$\lim_{\rho\to\pm\infty}\phi^1(\rho,t)=\varphi^0_r(\Gamma^0_\pm,t)+\varphi^1(\Gamma^0_\pm,t)=0. \tag{6.21}$$

The unique positive solution (up to translation) of (6.20),(6.21) is

$$\phi^1=\psi'. \tag{6.22}$$

Next, we study the $O(\epsilon^2)$ equation (6.19). Integrating twice and eliminating the terms at $-\infty$ as before, one obtains

$$L\phi^2\equiv\phi^2_{\rho\rho}+f'(\phi^0)\phi^2=-2U^0-f''(\phi^0)(\tfrac{1}{2}\phi^1)^2. \tag{6.23}$$

The solvability condition used in (4.27) now implies

$$\int_{-\infty}^{\infty}\psi'[-f''(\phi^0)(\tfrac{1}{2}\psi')^2-2U^0]\,d\rho=0. \tag{6.24}$$

Since f and f'' are odd, while f' and ψ' are even, (6.24) implies

$$4U^0=0. \tag{6.25}$$

By the first matching relation (3.7), one then has (6.3), to first order. This completes the second of three conditions. The latent heat conditions (6.2) can be derived in various ways, each of which is basically a consequence of (6.8) with $\varphi^0=\pm1$. Although the matching conditions can be used to derive this, one must follow the procedure to third order in ϵ in this case. Alternatively, one can write, in the (r,s) coordinates,

$$(u^0_t+r_tu^0_r+s_tu^0_s)+\tfrac{1}{2}l(\varphi^0_t+r^0_t\varphi^0_r+s^0_t\varphi^0_s)=K(u^0_{rr}+\kappa^0u^0_r+|\nabla s^0|^2u^0_{ss}+\Delta s^0u^0_s). \tag{6.26}$$

If one considers the equation

$$w_t-Kw_{rr}=-\tfrac{1}{2}\varphi^0_r, \tag{6.27}$$

then $\varphi_r^0 \in H^{-\frac{1}{2}-\epsilon}$ implies w will be in $H^{\frac{3}{2}-\epsilon}$, so that w will be continuous but may have a discontinuous gradient. Now we integrate (6.26), $\int_0^r d\bar{r}$ and $\int_r^0 d\bar{r}$, for some positive r, and subtract the difference. Then taking the limit as r approaches zero, the terms u and tangential derivatives vanish, leaving just the $\frac{1}{2} l r_t^0 \varphi_t^0$ and κu_{rr}^0 terms with the result

$$-lv^0 = K[u_r^0]_-^+. \tag{6.28}$$

This completes verification of Proposition 6.1.

7. The Hele–Shaw or quasi-static limit

We now consider a limit in which one has the steady-state form of the heat equation. The resulting equations (7.2)–(7.4) have been used (with u as pressure) to study the interface between two fluids sandwiched between plates of glass [10]. In terms of phase transitions, these equations are sometimes called quasi-static because the latent heat is taken into account explicitly at the interface but diffusion of heat occurs instantaneously. These equations were used particularly in the early studies of instabilities of an interface (Mullins–Sekerka). We consider first the following scaling of (1.2),(1.6):

$$\epsilon \equiv a = \xi^2, \qquad \tau = \epsilon, \qquad l = c_1^2 \xi^{-2}, \qquad K = c_2^2 \xi^{-2}, \tag{7.1}$$

noting that the scaling of τ is not crucial so long as $\tau = o(1)$.

PROPOSITION 7.1 *In the limit as ξ approaches zero in accordance with the scaling of* (7.1), *there exist formal asymptotic solutions to the conserved phase field equations* (1.2),(1.6) *subject to the boundary conditions of Section* 3 *which are governed in a formal asymptotic sense by the Hele–Shaw equations*

$$\Delta u = 0 \quad \text{in } \Omega_\pm, \tag{7.2}$$

$$[\nabla u]_-^+ = -\tfrac{1}{2}(c_1/c_2)^2 v \quad \text{on } \Gamma, \tag{7.3}$$

$$u = -\tfrac{1}{4}\sigma\kappa \quad \text{on } \Gamma. \tag{7.4}$$

The equations (1.2),(1.6) *can be written in this scaling as*

$$\frac{\epsilon}{c_2^2} u_t + \tfrac{1}{2}(c_1/c_2)^2 \varphi_t = \Delta u, \tag{7.5}$$

$$-\epsilon^3 \varphi_t = \epsilon^2 \Delta [\epsilon^2 \Delta \varphi + f(\varphi) + 2\epsilon u]. \tag{7.6}$$

We write the inner and outer expansions as in Section 4.

The Outer Expansion

$O(1)$:

$$\tfrac{1}{2}(c_1/c_2)^2 \varphi_t^0 = \Delta u^0, \tag{7.7}$$

$$0 = \Delta f(\varphi^0). \tag{7.8}$$

Noting that (7.8) is identical to (4.5), we conclude $\varphi^0 = \pm 1$ on $\Omega_\pm$ as in (4.8). This immediately yields (7.2).

$O(\epsilon)$:

$$\frac{1}{c_2^2} u_t^0 + \tfrac{1}{2}(c_1/c_2)^2 \varphi_t^1 = \Delta u^1, \tag{7.9}$$

$$-\varphi_t^0 = \Delta[f'(\varphi^0)\varphi^1 + 2u^0]. \tag{7.10}$$

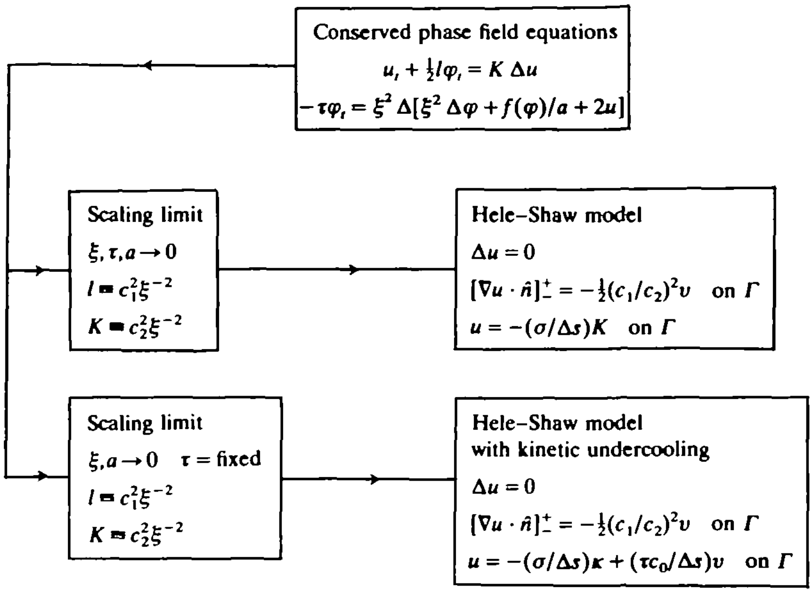

FIG. 2. Hele-Shaw (or quasi-static) models as limiting cases of the conserved phase field equations.

Since φ_t^0 vanishes ($r \neq 0$), one can write (7.10) as

$$\varphi^1 = -2\,\Delta\, u^0/f'(\varphi^0), \tag{7.11}$$

so that φ^1 and consequently u^1 can be obtained.

The Inner Expansion

Using the stretched variable $\rho = r/\epsilon$, we write

$$\tfrac{1}{2}(c_1/c_2)^2(\phi_t + \phi_r r_t + s_t \phi_s) = U_{rr} + \kappa U_r + |\nabla s|^2\, U_{ss} + \Delta s U_s, \tag{7.12}$$

$$-\epsilon^3(\phi_t + \phi_r r_t + s_t \phi_s) = \frac{\partial^2}{\partial \rho^2}[\phi_{\rho\rho} + f(\phi)]$$
$$+ \epsilon\left(\frac{\partial^2}{\partial \rho^2}(\kappa\phi_\rho + 2U) + \kappa\frac{\partial}{\partial\rho}[\phi_{\rho\rho} + f(\phi)]\right) + O(\epsilon^2), \tag{7.13}$$

which leads to the following balance of terms.

$O(1)$:
$$U_{\rho\rho} = 0, \tag{7.14}$$

$$\frac{\partial^2}{\partial\rho^2}[\phi_{\rho\rho} + f(\phi)] = 0. \tag{7.15}$$

The analysis of these is identical to that of Section 4 with the conclusion that $\phi^0 = \psi$ (equations (4.23),(4.24)) and U^0 is independent of ρ:

$O(\epsilon)$
$$\tfrac{1}{2}(c_1/c_2)\phi_\rho^0 r_t^0 = U_{\rho\rho}^1, \tag{7.16}$$

$$0 = \frac{\partial^2}{\partial\rho^2}\left(\frac{\partial^2\phi^1}{\partial\rho^2} + f'(\phi^0)\phi^1 + \kappa^0\phi_\rho^0 + 2U^0\right). \tag{7.17}$$

Since these equations are identical to (4.17),(4.18), the analysis of (4.25)–(4.32) leads to the latent heat condition (7.3) and the interface condition (7.4). This verifies Proposition 7.1.

One can obtain a modification of this limit by letting $\tau = O(1)$. The net result is that the condition (7.4) is replaced by

$$u = -\tfrac{1}{4}\sigma\kappa + \tfrac{1}{4}\tau c_0 v \quad \text{on } \Gamma. \tag{7.18}$$

8. The zero latent heat limit: the Cahn–Hilliard equation for spinodal decomposition

We now consider the equations (1.2),(1.6) with the aim of eliminating the role of the temperature, i.e. (1.2). In particular, we expect that, when the temperature is constant (in time and space), for example, and latent heat is zero, then equations (1.2),(1.6) reduce to a single equation which describes spinodal decomposition (Cahn–Hilliard [12]). We consider a more general situation for the temperature which includes constant temperature as a special case. Let the initial and boundary conditions (3.10),(3.13) be defined so that

$$u(0, x) = u_0(x) \quad \text{with } \Delta u_0(x) = 0, \tag{8.1}$$

$$\frac{\partial u}{\partial v}(t, x) = \frac{\partial u_0}{\partial v}(x) \quad (x \in \partial\Omega), \tag{8.2}$$

while the boundary conditions on φ are defined by (3.11),(3.12).

We consider the problem in which there is no latent heat, that is,

$$l = 0, \tag{8.3}$$

so that equation (1.2) is just the heat equation with no source term

$$u_t - K\,\Delta\, u = 0. \tag{8.4}$$

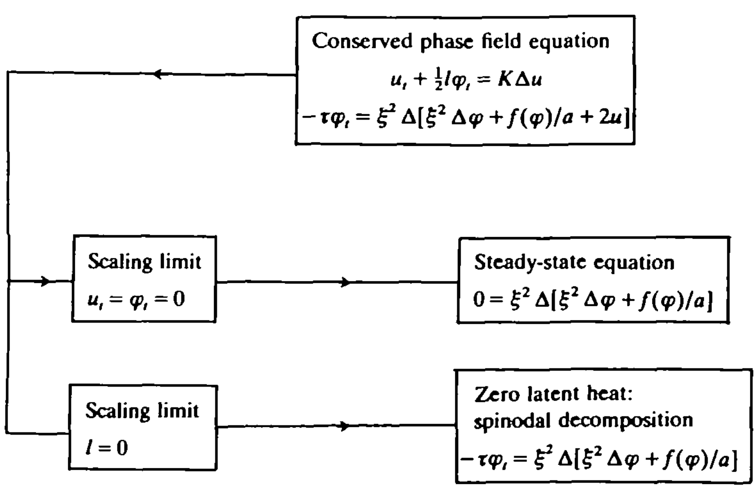

FIG. 3. Single equation limits of the conserved phase field equations.

Then uniqueness for the heat equation implies that

$$u(t, x) = u_0(x) \tag{8.5}$$

is the only solution to (8.4),(8.1),(8.2). Since $\Delta u = 0$ for all t, equation (1.6) is now just

$$-\tau\varphi_t = \xi^2 \Delta [\xi^2 \Delta \varphi + f(\varphi)/a]. \tag{8.6}$$

The asymptotics of moving internal layers are then an immediate consequence of Sections 4 or 5, depending on the scaling.

If we consider boundary conditions (3.12) and

$$\frac{\partial}{\partial \nu}[\xi^2 \Delta \varphi + a^{-1} f(\varphi)] = 0 \quad \text{on } \partial_\pm \Omega, \tag{8.7}$$

where Ω is a spherical annulus, then the order parameter is conserved globally and one finds that a single transitional layer can have only zero velocity. Clearly, any other result for these boundary conditions and geometry would violate global conservation.

In the limit we have considered here, the role of the temperature is eliminated and one obtains the Cahn–Hilliard equation in which the effect of limited growth due to latent heat has not had a chance to take effect. The internal layers thus obtained are consistent with known results in this case [14].

9. Conclusions

Having shown that a number of the macroscopic free-boundary problems arise from the conserved phase field equations (1.2),(1.6), we compare these with the nonconserved equations. In the steady-state situation, the macroscopic limit, that is,

$$\Delta u = 0 \quad \text{in } \Omega_\pm, \tag{9.1}$$

$$u = -\frac{\sigma}{\Delta s}\kappa \quad \text{on } \Gamma, \tag{9.2}$$

is the same as in the nonconserved case. We note that the existence of solutions to (9.1),(9.2) has been proved [20]. In the dynamical cases, we find that the coefficient of the undercooling term, i.e. $\tau c_0/\Delta s$ in (5.6), differs from the nonconserved case, in sign and magnitude under the boundary conditions considered, while the coefficient of the curvature remains the same. In view of stability studies on the macroscopic equations (see e.g. [21]), the stability properties of the conserved and nonconserved equations will differ. Sections 4–7 are to be compared with analogous results for the nonconserved equations [8]. They provide an answer to the question of how much difference the conserved or nonconserved order parameter makes in a dynamical setting. Except for the coefficient of the velocity term, the differences are at the level beyond the first order (i.e. macroscopic limit).

The asymptotic connection established between phase transition problems (equations (1.2),(1.6)) and spinodal decomposition (8.6) may provide a perspective in understanding the question introduced in [12: p. 800]:

'We cannot say much about the actual rate of spinodal decomposition except to place an upper limit on it. ... it is unlikely that this mechanism of spinodal decomposition will be observed near the limit of metastability, for it is too slow there, and long before it will have a chance, ordinary nucleation and growth resulting from finite fluctuations not permitted by equation (18) will have taken over.'

For any material under study, presumably one knows at least the order of magnitude of the surface tension σ and relaxation time τ. The range of validity of (8.6) for any transition rests on this calculation.

Setting $l = 0$ in (1.2) can be interpreted to mean that the time-scale governing (1.6) is many orders of magnitude shorter than that of (1.2). If this is consistent for a particular material, then this limit represents the 'crossover behaviour' from one stage to another.

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