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**Two-Phase Binary Fluids and
Immiscible Fluids Described by an
Order Parameter**

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TWO-PHASE BINARY FLUIDS AND IMMISCIBLE FLUIDS DESCRIBED BY AN ORDER PARAMETER

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A unified framework for coupled Navier-Stokes/Cahn-Hilliard equations is developed using, as a basis, a balance law for microforces in conjunction with constitutive equations consistent with a mechanical version of the second law. As a numerical application of the theory, we consider the kinetics of coarsening for a binary fluid in two space-dimensions.

1. INTRODUCTION

The Cahn-Hilliard equation (Cahn 1961)

$$\varphi' = m\Delta[f'(\varphi) - \alpha\Delta\varphi] \quad (1.1)$$

is central to materials science, as it characterizes important qualitative features of two-phase systems. This equation is based on a free energy

$$\hat{\psi}(\varphi, \nabla\varphi) = f(\varphi) + \frac{1}{2}\alpha|\nabla\varphi|^2, \quad (1.2)$$

with $f(\varphi)$ a double-well potential whose wells define the phases, and leads to an interfacial layer within which the density φ suffers large variations.

The standard derivation of the Cahn-Hilliard equation begins with the mass balance

$$\varphi' = -\operatorname{div} h \quad (1.3)$$

and the constitutive equation

$$h = -m\nabla\mu, \quad (1.4)$$

which relates the mass flux h to the chemical potential μ . The presence of density gradients renders (1.2) incompatible with the classical definition of μ as the partial derivative of ψ with respect to φ ; instead μ is defined as the variational derivative $\mu = \delta\Psi/\delta\varphi$ of the total free energy

$$\Psi(\varphi) = \int_B \hat{\Psi}(\varphi, \nabla\varphi) dv \quad (B = \text{underlying region of space}). \quad (1.5)$$

Since

$$\delta\Psi/\delta\varphi = f'(\varphi) - \alpha\Delta\varphi, \quad (1.6)$$

this yields the Cahn-Hilliard equation.

The major advances in nonlinear continuum mechanics over the past thirty years are based on the separation of balance laws (such as those for mass and force), which are general and hold for large classes of materials, from constitutive equations (such as those for elastic solids and viscous fluids), which delineate specific classes of material behavior. In the derivation presented above there is no such separation, and it is not clear whether there is an underlying balance law that can form a basis for more general theories.

An alternative derivation of the Cahn-Hilliard equation (Gurtin 1995) is based on a balance law for microforces (Fried & Gurtin 1993), defined operationally as forces whose working accompanies changes in φ . These forces are described by a (vector) stress ξ , which characterizes forces transmitted across surfaces, and a (scalar) body force π , which represents internal forces distributed over the volume of the material. The basic hypothesis is the microforce balance

$$\int_{\partial R} \xi \cdot n da + \int_R \pi dv = 0 \quad (1.7)$$

for each control volume R , with n the outward unit normal to ∂R .

Here we study the isothermal motion of an incompressible binary fluid, with one of the constituent densities serving as the order parameter. A chief assumption is that the relative momenta and kinetic energies of the constituents are

negligible when computed relative to the gross motion of the fluid. This allows us to base the theory on:

- balance of mass for the order parameter;
- the microforce balance (1.7);
- balance of momentum for the macroscopic motion of the fluid;
- a version of the second law in the form of a global free-energy inequality in which the microscopic working (Fried & Gurtin 1993)

$$\int_{\partial R} \varphi \cdot \xi \cdot n \, da \quad (1.8)$$

joins the working of the macroscopic stresses; and

- constitutive equations presumed compatible with this version of the second law.

In standard theories of diffusion the chemical potential is given, constitutively, as a function of the density, but here we consider systems sufficiently far from equilibrium that a relation of this type is no longer valid; instead we allow the chemical potential and its gradient to join the stretching tensor, the density, and the density gradient as independent constitutive variables. Interestingly, the second law reduces the free energy to a function $\psi = \hat{\psi}(\varphi, \text{grad}\varphi)$ of at most φ and $\text{grad}\varphi$, where $\text{grad}\varphi$ denotes the spatial (Eulerian) gradient.

A chief result of our theory is a constitutive equation giving the macroscopic (Cauchy) stress as a classical Newtonian stress plus a term

$$\alpha \text{grad}\varphi \otimes \text{grad}\varphi, \quad (1.9)$$

which represents capillarity.¹ Our final results consist of the coupled Navier-Stokes/Cahn-Hilliard equations

$$\begin{aligned} \rho [\mathbf{v}_t + (\text{grad}\mathbf{v})\mathbf{v}] &= -\text{grad}p + \nu\Delta\mathbf{v} - \alpha(\Delta\varphi)\text{grad}\varphi, & \text{div}\mathbf{v} &= 0, \\ \varphi_t + (\text{grad}\varphi) \cdot \mathbf{v} &= m\Delta[f'(\varphi) - \alpha\Delta\varphi]. \end{aligned} \quad (1.10)$$

We also develop equations for the motion of immiscible fluids. Here our use of an order parameter endows the interface with capillarity and yields a theory in which the free-boundary need not be explicitly tracked; as this theory does not allow for a phase change, the interface is transported with the material.

The model defined by (1.10), which is referred to as "Model H" in the literature on critical phenomena (cf. Hohenber & Halperin 1977), was used by Siggia,

¹A term of this type appears in Korteweg's theory of gradient fluids (cf. Truesdell & Noll 1965, §124).

Halperin, & Hohenberg (1976) to study behavior at the critical points of single and binary fluids. Later extensions of the model were used to analyze the superfluid transition of ^4He (Pankert & Dohm 1981) as well as the decay of critical fluctuations in simple fluids (Onuki & Kawasaki 1979) and polymer solutions (Helfand & Fredrickson 1989) under an imposed shear flow. A chief purpose of these studies was to analyze the effect of reversible modes (i.e., those corresponding to the coupling terms $(\text{grad}\varphi)\cdot\mathbf{v}$ and $\alpha(\Delta\varphi)\text{grad}\varphi$) on the dynamical critical behavior of otherwise purely dissipative models, with emphasis placed on the behavior of hydrodynamic transport coefficients near the critical point. More recently, (1.10) was used to study other nonequilibrium phenomena below the critical point; for example, Kawasaki & Ohta (1983) and Koga & Kawasaki (1991) use (1.10) to study hydrodynamic effects during spinodal decomposition.

The applicability of (1.10) to studies of the type discussed above is generally based, not on first principles, but instead on the observation that a convective term $(\text{grad}\varphi)\cdot\mathbf{v}$ in the Cahn-Hilliard equation should be accompanied by a term $\alpha(\Delta\varphi)\text{grad}\varphi$ in the Navier-Stokes equation to ensure that the asymptotic probability-distribution functions obtained as $t\rightarrow\infty$ coincide with those given by standard equilibrium calculations. In view of the phenomenological nature of this formalism, it seems natural to ask whether there is a derivation of (1.10) within the framework of nonlinear continuum mechanics. Here we provide such a derivation.

In addition, we present computational results appropriate to a range of parameters in which sharp interfaces (large, localized changes in φ) exist.

From a computational standpoint our approach is similar to VOF (volume-of-fluid) methods (Hirt & Nichols 1981). There a color function, which plays a role similar to that of φ , is passively advected by the flow. More recently the VOF method has been extended to include capillary effects (Univerdi & Trygvasson 1992; Haj-Hariri, Shi & Borhan 1994) leading to a modified Navier-Stokes equation equivalent to the first of (1.10). These models, however, do not endow the color function with any physical significance, and dissipative relaxation as in the equation for φ in (1.10) is absent. In comparison, not only does the model based on (1.10) include capillary effects in the modified Navier-Stokes equation, it also explicitly includes other dissipative processes up to the length scale of the smeared interface; it can therefore describe events such as break-up and coalescence, with the proviso that the physical behavior at those length scales is determined by the choice of free energy ψ .

Notation. Tensors are linear transformations of \mathbb{R}^3 into \mathbb{R}^3 and are denoted by upper-case boldface letters. Vectors may be viewed as 3×1 column vectors and tensors as 3×3 matrices. $\mathbf{1}$ denotes the unit tensor; $\mathbf{a}\otimes\mathbf{b}$, the tensor product of

vectors \mathbf{a} and \mathbf{b} , is the tensor defined by $(\mathbf{a} \otimes \mathbf{b})\mathbf{u} = (\mathbf{b} \cdot \mathbf{u})\mathbf{a}$ for all vectors \mathbf{u} ; \mathbf{A}^T is the transpose of a tensor \mathbf{A} ; $\text{tr}\mathbf{A}$ is the trace of \mathbf{A} ; the inner product of tensors \mathbf{A} and \mathbf{B} is defined by $\mathbf{A} \cdot \mathbf{B} = \text{tr}(\mathbf{A}^T \mathbf{B})$.

The divergence, gradient, and Laplacian of a field $\varphi = \varphi(\mathbf{x}, t)$ are denoted by $\text{grad}\varphi$, $\text{div}\varphi$, and $\Delta\varphi$. For a vector field $\mathbf{u}(\mathbf{x})$, $\text{grad}\mathbf{u}(\mathbf{x})$ is the tensor with components $\partial u_i / \partial x_j$ (i = row index, j = column index). The divergence of a tensor field $\mathbf{A}(\mathbf{x})$ is the vector field with components $\sum_j \partial A_{ij} / \partial x_j$ (i = row index).

The derivative of a function f of a scalar variable (not time) is denoted by a prime: f' . The partial derivative of a function $\mathfrak{F}(a, b, c, \dots, d)$ (of n scalar, vector, or tensor variables) with respect to b , say, is written $\partial_b \mathfrak{F}(a, b, c, \dots, d)$.

2. BASIC LAWS

We consider the isothermal motion of an incompressible binary fluid whose total density is constant. A basic assumption of our theory is that *the momenta and kinetic energies of the constituents are negligible when computed relative to the gross motion of the fluid.*

a. Kinematics

We write grad and div the spatial gradient and spatial divergence. Incompressibility then requires that \mathbf{v} , the gross velocity of the fluid, satisfy

$$\text{div}\mathbf{v} = \text{tr}(\text{grad}\mathbf{v}) = 0, \quad (2.1)$$

a constraint that renders the stretching,

$$\mathbf{D} = \frac{1}{2}(\text{grad}\mathbf{v} + \text{grad}\mathbf{v}^T), \quad (2.2)$$

traceless.

We will use both the spatial time derivative $(\dots)_t$ and the material time derivative $(\dots)^\cdot$; these are related through

$$(\dots)^\cdot = (\dots)_t + [\text{grad}(\dots)]\mathbf{v}. \quad (2.3)$$

We will also use the following identity for scalar fields φ :

$$\text{grad}(\varphi^\cdot) = (\text{grad}\varphi)^\cdot + (\text{grad}\mathbf{v})^T \text{grad}\varphi. \quad (2.4)$$

b. Balance of mass

We write ρ_b for the density and h_b for the mass flux of constituent b ($= 1, 2$),

with h_b measured relative to the gross motion of the fluid. Then

$$\rho_1 + \rho_2 = \rho \quad (2.5)$$

with ρ , the total density of the fluid, constant; consistent with this constraint, we assume that

$$h_1 + h_2 = 0. \quad (2.6)$$

Throughout the paper R denotes an arbitrary control volume (fixed region of space), with n the outward unit normal to ∂R . Given a field Φ ,

$$\left\{ \int_R \Phi dv \right\}' = \int_R \Phi' dv \quad (2.7)$$

where the dot signifies the time derivative following the material currently in R , and where the integral and time derivative commute by virtue of balance of mass, since the total density of the fluid is constant.

Balance of mass requires that

$$\left\{ \int_R \rho_b dv \right\}' = - \int_{\partial R} h_b \cdot n da \quad (2.8)$$

for each constituent b . Because of (2.5) and (2.6), one of the two relations (2.8) is redundant; we therefore let

$$\varphi = \rho_1, \quad h = h_1, \quad (2.9)$$

and restrict attention to the local balance

$$\varphi' = - \operatorname{div} h \quad (2.10)$$

for the first constituent.

c. Balance of momentum

We write T for the stress tensor associated with the macroscopic motion of the fluid. Then, since we neglect the relative momenta of the constituents, the balance laws for linear and angular momentum have the standard form

$$\int_{\partial R} \mathbf{T} \mathbf{n} \, da = \left\{ \int_R \rho \mathbf{v} \, dv \right\}', \quad \int_{\partial R} \mathbf{x} \times \mathbf{T} \mathbf{n} \, da = \left\{ \int_R (\mathbf{x} \times \rho \mathbf{v}) \, dv \right\}' \quad (2.11)$$

for each R , or equivalently,

$$\operatorname{div} \mathbf{T} = \rho \mathbf{v}', \quad \mathbf{T} = \mathbf{T}^T. \quad (2.12)$$

It is convenient to introduce the extra stress \mathbf{S} and the pressure p defined by

$$\mathbf{S} = \mathbf{T} + p \mathbf{1}, \quad p = -\frac{1}{3}(\operatorname{tr} \mathbf{T}). \quad (2.13)$$

As a consequence of incompressibility, p is indeterminate.

d. Order parameter. Microforce balance

We assume that the microscopic behavior of the fluid, as manifested in the diffusion of its constituents, is described by a scalar order-parameter ω and concomitant microforces whose working accompanies changes in ω . Since working is characterized by terms of the form {microforce times ω' }, microforces are here scalar quantities. Precisely, we assume that the microforces are described by a (vector) stress $\boldsymbol{\xi}$ —whose traction $\boldsymbol{\xi} \cdot \mathbf{n}$ characterizes forces transmitted across oriented surfaces of unit normal \mathbf{n} —in conjunction with a (scalar) body force π , which represents internal forces distributed over the volume of the fluid; these forces are presumed consistent with the microforce balance (Fried & Gurtin 1993)

$$\int_{\partial R} \boldsymbol{\xi} \cdot \mathbf{n} \, da + \int_R \pi \, dv = 0 \quad (2.14)$$

for each control volume R , or equivalently

$$\operatorname{div} \boldsymbol{\xi} + \pi = 0. \quad (2.15)$$

A basic hypothesis of the theory is an identification of the order parameter ω with the constituent density φ :

$$\omega = \varphi. \quad (2.16)$$

e. Second law in the form of a dissipation inequality

We restrict attention to isothermal behavior and therefore consider a mechanical version of the second law: for each control volume R , the rate at which the

energy of R increases cannot exceed the working on R plus the rate at which energy is transported to R by diffusion. Let μ_b denote the chemical potential of constituent b, and let

$$\mu = \mu_1 - \mu_2. \quad (2.17)$$

Then

$$-\sum_{b=1,2} \int_{\partial R} \mu_b h_b \cdot n \, da = - \int_{\partial R} \mu h \cdot n \, da \quad (2.18)$$

represents energy carried into R across ∂R by diffusion, while

$$\int_{\partial R} Tn \cdot v \, da, \quad \int_{\partial R} \varphi^* \xi \cdot n \, da \quad (2.19)$$

gives the working of the macroscopic and microscopic stresses. Thus, since we neglect the relative kinetic energy of the constituents, the appropriate form of the second law is the dissipation inequality

$$\left\{ \int_R (\psi + k) \, dv \right\}' \leq \int_{\partial R} Tn \cdot v \, da + \int_{\partial R} \varphi^* \xi \cdot n \, da - \int_{\partial R} \mu h \cdot n \, da, \quad (2.20)$$

where $k = \frac{1}{2} \rho v^2$. The body force π does not contribute, since it acts internally to R.

By (2.6), (2.10), (2.12), and (2.15), (2.20) has the local form

$$\psi^* - T \cdot \text{grad} v + (\pi - \mu) \varphi^* + \xi \cdot \text{grad}(\varphi^*) + h \cdot \text{grad} \mu \leq 0. \quad (2.21)$$

Combining (2.21) with (2.4), (2.11), and (2.13), we are led to a local dissipation inequality

$$\psi^* - [S + (\text{grad} \varphi) \otimes \xi] \cdot \text{grad} v + (\pi - \mu) \varphi^* - \xi \cdot (\text{grad} \varphi)^* + h \cdot \text{grad} \mu \leq 0 \quad (2.22)$$

that will form a basis for our discussion of constitutive equations.

The negative of the left side of (2.22) represents the dissipation \mathcal{D} , as its integral over R is the right side of (2.20) minus the left. Thus, for motion in a container B with $v = 0$ and $\varphi^* \xi \cdot n = 0$ on ∂B ,

$$\left\{ \int_B (\psi + k) dv \right\}' = - \int_B \mathcal{D} dv \leq 0 \quad \text{if } \mathbf{h} \cdot \mathbf{n} = 0 \text{ on } \partial B, \quad (2.23)$$

$$\left\{ \int_B (\psi - \mu_0 \rho + k) dv \right\}' = - \int_B \mathcal{D} dv \leq 0 \quad \text{if } \mu = \mu_0 = \text{const. on } \partial B.$$

The thermodynamic development therefore yields natural Lyapunov functions for certain classes of flows.

3. CONSTITUTIVE EQUATIONS. RESTRICTIONS IMPOSED BY THE SECOND LAW

In standard theories of diffusion the chemical potential is given, constitutively, as a function of the density, but here we consider systems sufficiently far from equilibrium that a relation of this type is no longer valid; instead we allow the chemical potential and its gradient to join the stretching, the density, and the density gradient in the list of constitutive variables. Precisely, we consider constitutive equations of the form

$$\begin{aligned} \psi &= \hat{\psi}(D, \varphi, \text{grad } \varphi, \mu, \text{grad } \mu), \\ \mathbf{S} &= \hat{\mathbf{S}}(D, \varphi, \text{grad } \varphi, \mu, \text{grad } \mu), \\ \boldsymbol{\xi} &= \hat{\boldsymbol{\xi}}(D, \varphi, \text{grad } \varphi, \mu, \text{grad } \mu), \\ \pi &= \hat{\pi}(D, \varphi, \text{grad } \varphi, \mu, \text{grad } \mu), \\ \mathbf{h} &= \hat{\mathbf{h}}(D, \varphi, \text{grad } \varphi, \mu, \text{grad } \mu), \end{aligned} \quad (3.1)$$

with each of the constitutive functions isotropic, since the material is a fluid. To avoid notation such as $\partial_{\text{grad } \varphi} \hat{\psi}(D, \varphi, \text{grad } \varphi, \mu, \text{grad } \mu)$ for the partial derivative with respect to $\text{grad } \varphi$, we write

$$\mathbf{b} = \text{grad } \varphi, \quad \mathbf{s} = \text{grad } \mu. \quad (3.2)$$

Not all constitutive relations of the form (3.1) are admissible, as without further restrictions (3.1) will violate the dissipation inequality (2.22). To determine the requisite restrictions we choose arbitrary fields \mathbf{v} , φ , and μ for the velocity, order parameter, and chemical potential, and use (3.1) to compute a constitutive process consisting of \mathbf{v} , φ , μ and the fields ψ , \mathbf{S} , $\boldsymbol{\xi}$, π , and \mathbf{h} ; such a constitutive process will satisfy (2.22) if and only if

$$\begin{aligned}
 & [\partial_D \hat{\psi}(\dots)] \cdot D' + [\partial_\varphi \hat{\psi}(\dots) + \hat{\pi}(\dots) - \mu] \varphi' + [\partial_b \hat{\psi}(\dots) - \hat{\xi}(\dots)] \cdot b' - \\
 & [\hat{S}(\dots) + b \otimes \hat{\xi}(\dots)] \cdot \text{grad } v + \\
 & [\partial_\mu \hat{\psi}(\dots)] \mu' + [\partial_s \hat{\psi}(\dots)] \cdot s' + \hat{h}(\dots) \cdot s \leq 0,
 \end{aligned} \tag{3.3}$$

where we have written (...) as shorthand for the list of independent constitutive variables:

$$(\dots) = (D, \varphi, \text{grad } \varphi, \mu, \text{grad } \mu). \tag{3.4}$$

It is possible to find fields $v(x,t)$, $\varphi(x,t)$, and $\mu(x,t)$ such that v , $\text{grad } v$, $(\text{grad } v)'$, φ , φ' , $b = \text{grad } \varphi$, $b' = (\text{grad } \varphi)'$, μ , μ' , $s = \text{grad } \mu$, and $s' = (\text{grad } \mu)'$ have arbitrarily prescribed values at some chosen point and time.² Thus, since the terms D' , φ' , b' , μ' , and s' appear linearly in (3.3), it follows that $\partial_D \hat{\psi} = 0$, $\partial_\varphi \hat{\psi} = \mu - \hat{\pi}$, $\partial_\mu \hat{\psi} = 0$, $\partial_s \hat{\psi} = 0$, and $\partial_b \hat{\psi} = \hat{\xi}$. We are therefore led to the following constitutive restrictions:

- (i) the free energy and microstress are independent of D , μ , and $\text{grad } \mu$, and are related through

$$\hat{\xi}(\varphi, \text{grad } \varphi) = \partial_b \hat{\psi}(\varphi, \text{grad } \varphi); \tag{3.5}$$

- (ii) the internal microforce is independent of D and $\text{grad } \mu$ and represents a nonequilibrium contribution to the chemical potential:

$$\hat{\pi}(\varphi, \text{grad } \varphi, \mu) = \mu - \partial_\varphi \hat{\psi}(\varphi, \text{grad } \varphi); \tag{3.6}$$

- (iii) the following inequality must be satisfied for all values of the arguments:

$$\hat{h}(\dots) \cdot \text{grad } \mu - [\hat{S}(\dots) + b \otimes \hat{\xi}(\varphi, \text{grad } \varphi)] \cdot \text{grad } v \leq 0. \tag{3.7}$$

Since the skew part of $\text{grad } v$ can be chosen arbitrarily and independently of

²It is tacit that there are external mass supplies and forces available to ensure satisfaction of the balance laws for arbitrary choices of the fields v , φ , and μ . We chose not to introduce external fields (source terms) since they tend to complicate the discussion and since it is only here that they are required. Specifically, we need an external mass supply r and external body forces b and γ such that (2.10), (2.12), and (2.15) become $\varphi' = -\text{div } h + r$, $\text{div } T + b = \rho v'$, and $\text{div } \xi + \pi + \gamma = 0$, and such that the dissipation inequality (2.20) contains the additional term $\int_R (b \cdot v + \varphi' \gamma + \mu r) dv$ on the right side. Allowing an external supply for each balance law is an assumption now standard in continuum mechanics; such assumptions are, of course, tacit in derivations dependent upon arbitrary variations of a field.

D , and since S is symmetric, $\xi = \hat{\xi}(\varphi, \mathbf{b})$ satisfies

$$\mathbf{b} \otimes \xi = \xi \otimes \mathbf{b}, \quad (\mathbf{b} \cdot \xi) \mathbf{b} = |\mathbf{b}|^2 \xi \quad (3.8)$$

and is hence parallel to \mathbf{b} . Further, the isotropy of $\xi = \hat{\xi}(\varphi, \mathbf{b})$ implies that $\xi = 0$ when $\mathbf{b} = 0$; hence there is a scalar function $\alpha(\varphi, \mathbf{b})$ such that

$$\xi = \alpha(\varphi, \mathbf{b}) \mathbf{b}. \quad (3.9)$$

Let

$$\mathbf{P} = \hat{\mathbf{P}}(\dots) = \hat{\mathbf{S}}(\dots) + \alpha(\varphi, \mathbf{b}) [\mathbf{b} \otimes \mathbf{b} - \frac{1}{3} |\mathbf{b}|^2 \mathbf{1}]; \quad (3.10)$$

then, since $\text{tr} D = 0$, (3.7) reduces to

$$\hat{\mathbf{h}}(\dots) \cdot \mathbf{s} - \hat{\mathbf{P}}(\dots) \cdot D \leq 0. \quad (3.11)$$

\mathbf{P} , in (3.11), represents a thermodynamic stress, as it is conjugate to the stretching D .

Any set of constitutive equations consistent with the restrictions (3.5), (3.6), (3.9), and (3.11) will be consistent with the dissipation inequality (2.22). Our purpose here is not to develop the most general theory possible, but rather to develop a theory that couples the essential features of the Cahn-Hilliard and Navier-Stokes equations. Newtonian fluids have stress linear in D , while Cahn-Hilliard diffusion has mass flux linear in $\text{grad} \mu$ and free energy quadratic in $\text{grad} \varphi$. Guided by these theories and by (3.11), we now assume that the thermodynamic stress \mathbf{P} , and the mass flux \mathbf{h} have the specific forms

$$\mathbf{P} = 2\nu(\varphi) D, \quad \mathbf{h} = -m(\varphi) \text{grad} \mu, \quad (3.12)$$

with mobility $m(\varphi)$ and viscosity $\nu(\varphi)$ nonnegative, and, appealing to (3.9), that the free energy ψ has the form

$$\psi = f(\varphi) + \frac{1}{2} \alpha(\varphi) |\text{grad} \varphi|^2 \quad (3.13)$$

with $\alpha(\varphi)$ nonnegative. Then

$$\begin{aligned}
 \mathbf{T} &= -p\mathbf{1} + 2\nu(\varphi)\mathbf{D} - \alpha(\varphi)\text{grad}\varphi \otimes \text{grad}\varphi, \\
 \boldsymbol{\xi} &= \alpha(\varphi)\text{grad}\varphi, \\
 \pi &= \mu - f'(\varphi) - \frac{1}{2}\alpha'(\varphi)|\text{grad}\varphi|^2,
 \end{aligned}
 \tag{3.14}$$

where, for convenience, the pressure p has been replaced by $p + (\alpha/3)|\text{grad}\varphi|^2$. If we assume, in addition, that α , m , and ν are constants, then

$$\begin{aligned}
 \psi &= f(\varphi) + \frac{1}{2}\alpha|\text{grad}\varphi|^2, \\
 \mathbf{T} &= -p\mathbf{1} + 2\nu\mathbf{D} - \alpha\text{grad}\varphi \otimes \text{grad}\varphi, \\
 \boldsymbol{\xi} &= \alpha\text{grad}\varphi, \\
 \pi &= \mu - f'(\varphi), \\
 \mathbf{h} &= -m\text{grad}\mu.
 \end{aligned}
 \tag{3.15}$$

The term $\alpha\text{grad}\varphi \otimes \text{grad}\varphi$ in the stress gives rise to normal stresses in the absence of flow; this term should represent surface tension and could effect boundary conditions at a free surface in a nonstandard manner.

Further, and what is most important, the microbalance (2.15) and the constitutive relation for π yield Cahn's formula for the chemical potential

$$\mu = f'(\varphi) - \alpha\Delta\varphi.
 \tag{3.16}$$

The basic PDEs of the theory follow upon substituting (3.15) and (3.16) into (2.10) and (2.12); the results, after replacing the original pressure p by $p - (\alpha/6)|\text{grad}\varphi|^2$, consist of generalized Navier-Stokes equations

$$\rho\mathbf{v}' = -\text{grad}p + \nu\Delta\mathbf{v} - \alpha(\Delta\varphi)\text{grad}\varphi, \quad \text{div}\mathbf{v} = 0,
 \tag{3.17}$$

coupled to the Cahn-Hilliard equation

$$\varphi' = m\Delta[f'(\varphi) - \alpha\Delta\varphi].
 \tag{3.18}$$

The latter equation depends explicitly on the flow velocity, since the material time derivatives have spatial forms:

$$\varphi' = \varphi_t + (\text{grad}\varphi) \cdot \mathbf{v}, \quad \mathbf{v}' = \mathbf{v}_t + (\text{grad}\mathbf{v})\mathbf{v}.
 \tag{3.19}$$

An interesting alternative form for these PDEs mentions the chemical poten-

tial explicitly:

$$\begin{aligned} \rho \mathbf{v}' &= -\text{grad} p + \nu \Delta \mathbf{v} + \mu \text{grad} \varphi, & \text{div} \mathbf{v} &= 0, \\ \varphi' &= m \Delta \mu, \\ \mu &= f'(\varphi) - \alpha \Delta \varphi, \end{aligned} \tag{3.20}$$

where the original pressure p has now been replaced by $p - (\alpha/6)|\text{grad} \varphi|^2 + f(\varphi)$.

4. IMMISCIBLE FLUIDS DESCRIBED BY AN ORDER PARAMETER

With but minor modifications the theory presented above can be applied to immiscible fluids. Here the order parameter φ has a given value in each fluid, with the fluid interface defined by the variation in φ between values. Since the fluids are immiscible, the interface should be transported with the fluid; we therefore require that

$$\varphi' = 0, \tag{4.28}$$

so that φ is constant on streamlines. Further, we let $\rho = \rho(\varphi)$, allowing the fluids to have different densities; this dependence on φ is consistent with incompressibility, since, by (4.28), $\rho(\varphi)' = 0$.

The microforce balance is no longer relevant; the basic equations are the classical balances (2.6) and the dissipation inequality

$$\left\{ \int_R (\psi + k) dv \right\}' \leq \int_{\partial R} \mathbf{T} \mathbf{n} \cdot \mathbf{v} da, \quad k = \frac{1}{2} \rho(\varphi) \mathbf{v}^2, \tag{4.29}$$

and this leads to the local dissipation inequality

$$\psi' - \mathbf{S} \cdot \text{grad} \mathbf{v} \leq 0. \tag{4.30}$$

As constitutive equations we assume that

$$\psi = \hat{\psi}(\mathbf{D}, \varphi, \text{grad} \varphi), \quad \mathbf{S} = \hat{\mathbf{S}}(\mathbf{D}, \varphi, \text{grad} \varphi), \tag{4.31}$$

and proceeding as before, consistency with (4.30) leads, by virtue of (2.4) and (4.28), to the inequality

$$[\partial_D \hat{\psi}(D, \varphi, \mathbf{b})] \cdot \mathbf{D} - [\hat{S}(D, \varphi, \mathbf{b}) + \mathbf{b} \otimes \partial_b \hat{\psi}(D, \varphi, \mathbf{b})] \cdot \text{grad} \mathbf{v} \leq 0, \quad (4.32)$$

rendering the free energy independent of \mathbf{D} . Finally, restricting attention to energies that are independent of φ and quadratic in $\text{grad} \varphi$, we are led to the constitutive equations

$$\begin{aligned} \psi &= \frac{1}{2} \alpha |\text{grad} \varphi|^2, \\ \mathbf{T} &= -p \mathbf{1} + 2\nu(\varphi) \mathbf{D} - \alpha \{ \text{grad} \varphi \otimes \text{grad} \varphi - \frac{1}{3} |\text{grad} \varphi|^2 \mathbf{1} \}. \end{aligned} \quad (4.33)$$

(A dependence of ψ on φ does not alter the resulting PDEs.)

The basic equations, after replacing p by $p - (\alpha/6)|\text{grad} \varphi|^2$, therefore have the form

$$\begin{aligned} \rho(\varphi) \mathbf{v}' &= -\text{grad} p + \nu(\varphi) \Delta \mathbf{v} + 2\nu'(\varphi) \mathbf{D} \text{grad} \varphi - \alpha (\Delta \varphi) \text{grad} \varphi, \\ \text{div} \mathbf{v} &= 0, \quad \varphi' = 0. \end{aligned} \quad (4.34)$$

These equations may be useful in the study of the interface between immiscible fluids; the order parameter automatically tracks the interface, here a layer, and provides a capillarity term $\alpha (\Delta \varphi) \text{grad} \varphi$ that hopefully models surface tension.

5. A NUMERICAL EXAMPLE: COARSENING

As a numerical application of the theory, we consider the kinetics of coarsening following a quench into the coexistence region of a binary fluid in two space-dimensions (see Mullins & Viñals 1989 for a review of coarsening). Numerical solutions of the Cahn-Hilliard equation *without* hydrodynamic effects have been obtained by a number of authors, for both critical (Gawliński, Viñals & Gunton 1989) and off-critical (Torralba, Chakraborti & Gunton 1989) quenches, while hydrodynamic effects on spinodal decomposition have been discussed by Koga & Kawasaki (1991). We consider here the off-critical region of the phase diagram in which the decay of the original state involves the formation and coarsening of localized droplets.

Our starting point is (3.17) and (3.18) with

$$f(\varphi) = -(r/2)\varphi^2 + (u/4)\varphi^4, \quad (5.1)$$

as the homogeneous part of the free energy density. For incompressible flows in two dimensions, it is convenient to introduce the stream function Ψ such that,

$$\mathbf{v} = (\partial_y \Psi) \mathbf{i} - (\partial_x \Psi) \mathbf{j}, \quad (5.2)$$

where \mathbf{i} and \mathbf{j} , respectively, are the unit vectors in the x and y directions. We next scale the order parameter by $(r/u)^{1/2}$, lengths by the the mean field correlation length $\xi = (\alpha/r)^{1/2}$, and time by the diffusion time $\tau = \alpha/mr^2$. In what follows, all variables are assumed to be dimensionless. Taking the curl of (3.17), and restricting attention to small Reynolds number ($Re = \xi^2 \rho / \nu \tau$), so that the inertial term in (3.17) is negligible, we obtain

$$\Delta^2 \Psi + C [\text{grad}(\Delta \varphi) \times \text{grad} \varphi] = 0, \quad (5.3)$$

where $C = \sigma \tau / \xi \nu$ plays the role of a capillary number, with $\sigma = \alpha r / u \xi$ the mean field value of the surface tension in this model. The fluid is enclosed in a square cavity of side L , with the fluid velocity satisfying no-slip boundary conditions on the walls of the cavity. Hence, the boundary conditions appropriate to (5.3) are that Ψ and its normal derivative $\partial \Psi / \partial n$ vanish on the boundary.

The dimensionless Cahn-Hilliard equation reads

$$\varphi_t + \mathbf{v} \cdot \text{grad} \varphi = -\Delta[\varphi - \varphi^3 + \Delta \varphi] \quad (5.4)$$

and is supplemented by the boundary conditions $\partial \varphi / \partial n = \partial \mu / \partial n = 0$, where $\mu = -[\varphi - \varphi^3 + \Delta \varphi]$.

The equations (5.3) and (5.4) are solved numerically in a square, two dimensional grid with a backward implicit method, and a fast biharmonic solver (details are given by Chella & Vinals 1994). We take $C=10$ and use the same parameters for the simulation as those of Toral, Chakrabarti & Gunton (1989) for a solution of the Cahn-Hilliard equation at an off-critical value of the order parameter: $L=256$, a grid spacing $\delta x=1.0$, and an initial configuration in which φ is random, gaussianly distributed with mean $\langle \varphi \rangle = 1/\sqrt{3}$ and unit variance. We choose a variable integration-step $\delta t=0.01$ for $0 \leq t < 4.0$, $\delta t=0.1$ for $4.0 < t \leq 664$ and $\delta t=0.5$ for $384 < t \leq 3700$.

Our results are summarized in Figures 1-3. At short times, drops of the minority phase are seen to nucleate, grow, and coarsen so as to decrease the free energy of the system. Figure 1 shows the distribution of phases—as defined by the dimensionless order-parameter—as a function of time; Figure 2 displays the corresponding distribution for the stream function. The main qualitative difference between our results and those for the uncoupled Cahn-Hilliard equation is

the flow-induced coalescence of neighboring droplets. The times in Figure 1 are chosen to illustrate coalescence. Figure 2 shows large and localized variations of the stream function in the regions in which coalescence is occurring. Coalescence is not observed in the purely relaxational Cahn-Hilliard equation; there coarsening can proceed only by diffusion.

Figure 3 graphs the total droplet-perimeter, per unit area (with the droplet boundaries defined as the level set $\phi=0$). At sufficiently long times growth is faster than the classical Lifshitz-Slyozov law (growth of the form $t^{1/3}$) for coarsening in the absence of hydrodynamic effects. Siggia (1979) predicted that hydrodynamic effects would affect coarsening, and San Miguel, Grant & Gunton (1985) adapted Siggia's argument to a two-dimensional system to obtain a growth law for the average droplet size proportional to $t^{1/2}$. The physical mechanism responsible for this growth law is droplet coalescence. Finally, molecular-dynamics simulations of coarsening in binary fluids (Leptoukh, Strickland & Roland 1994) have shown that the coalescence of droplets is the primary mechanism for growth.

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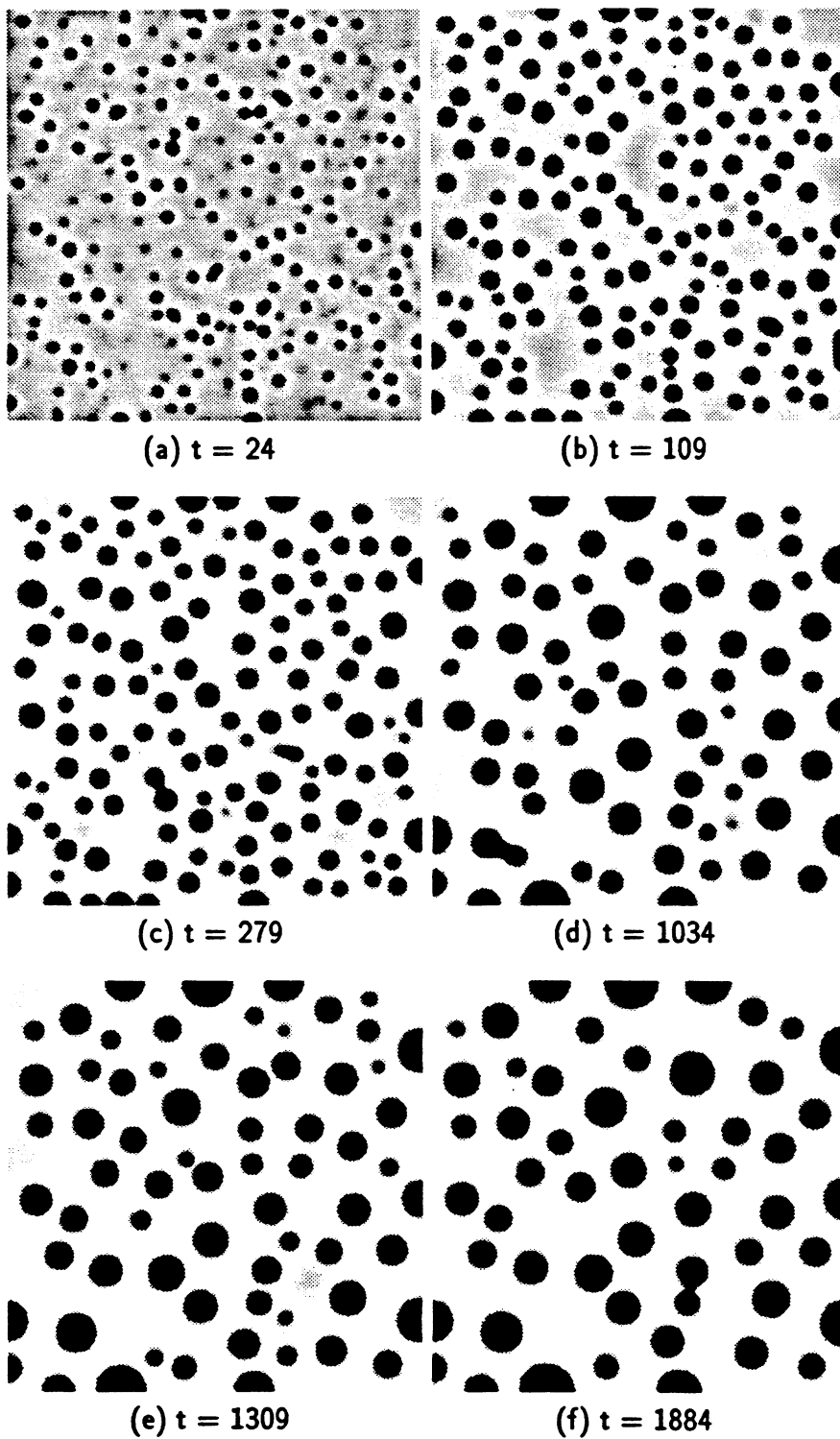
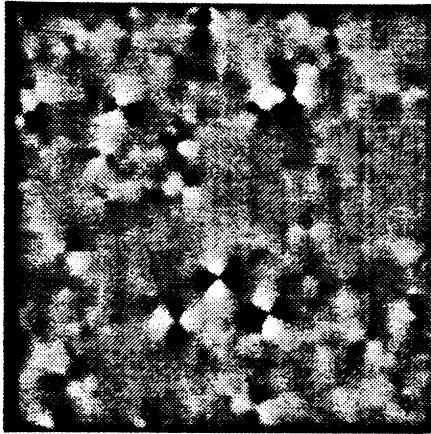
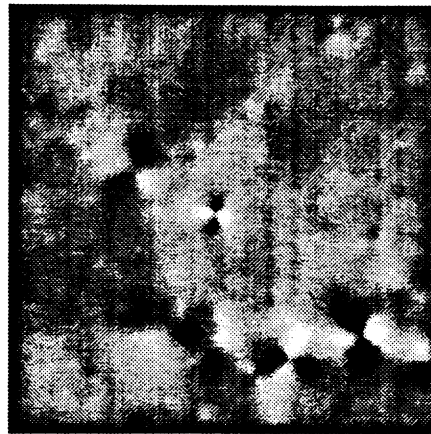


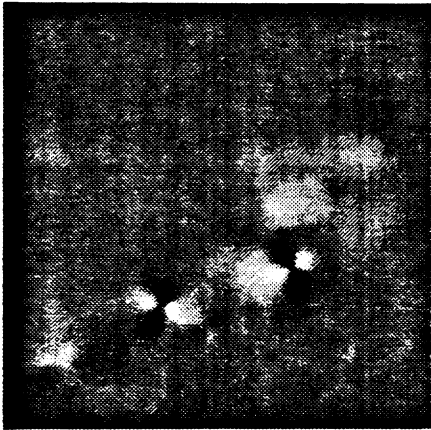
Figure 1, Gurtin et al.



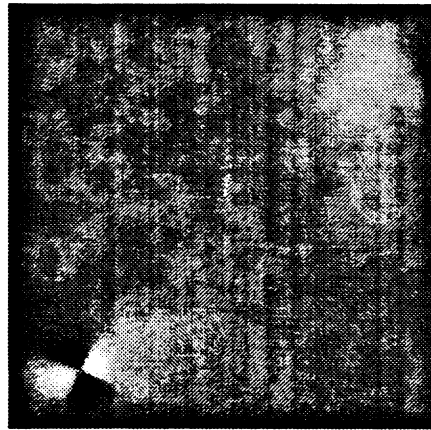
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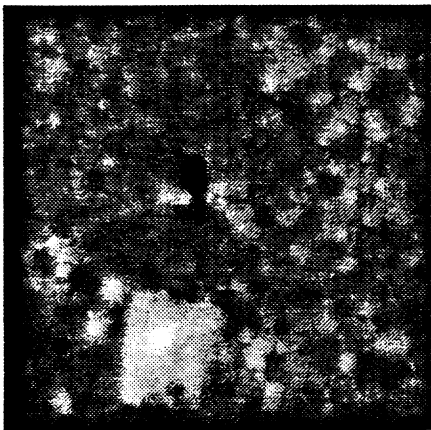
(b) $t = 109$



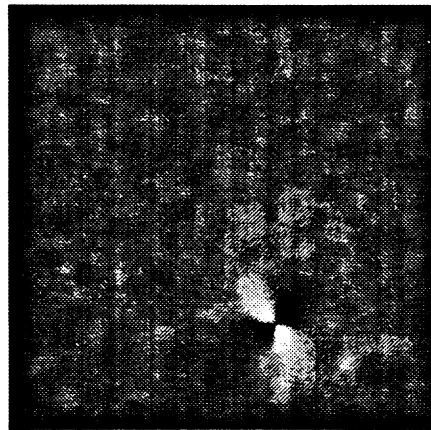
(c) $t = 279$



(d) $t = 1034$



(e) $t = 1309$



(f) $t = 1884$

Figure 2, Gurtin et al.

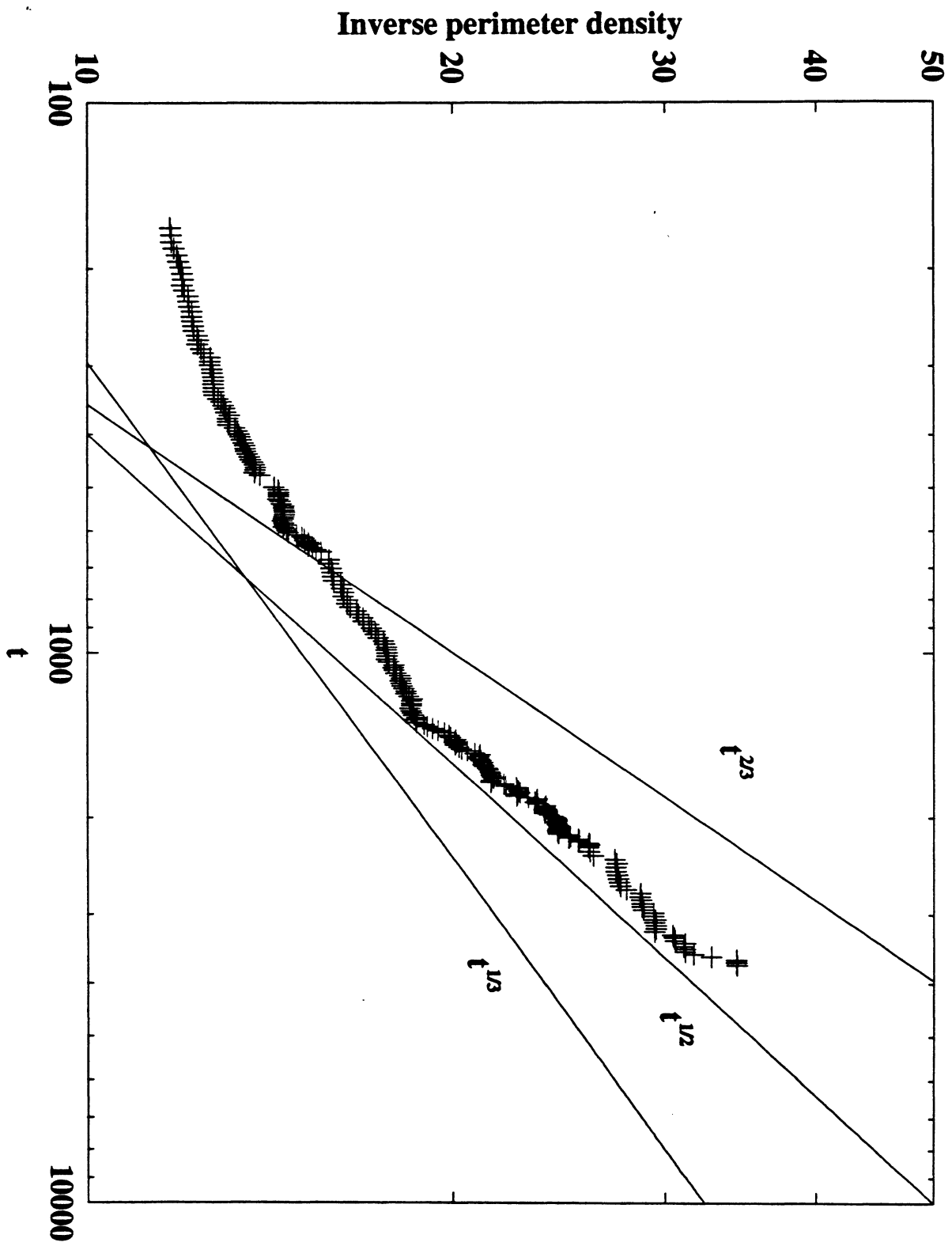


Figure 3, Gurtin et al.

FIGURE CAPTIONS

Figure 1. Order-parameter values (in grey scale) as a function of time showing nucleation and coarsening of the structure. Times have been chosen to highlight the coalescence of droplets.

Figure 2. Stream function Ψ in grey scale at the times shown in Figure 1. For the values of the parameters used, Ψ lies approximately between -0.5 and 0.5 . The regions of largest variation in the stream function are located in the regions where coalescence take place.

Figure 3. Inverse perimeter-density as a function of time for $C=10$. The three solid lines indicate power laws with the value of the exponent shown.

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