

A Derivation of a Phase Field Model with Fluid Properties

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Abstract. We extend the basic phase field model to physical problems in which fluid properties, such as velocity, pressure and density variations, are incorporated along with heat properties within the context of a unified and consistent derivation. One thereby obtains a system of parabolic differential equations with the variables temperature, phase, fluid velocity, density and pressure. The constants in the equations can be related to a rate constant and to equilibrium values in the pure phases.

1. INTRODUCTION

The motion of phase boundaries has been studied from a variety of physical and mathematical perspectives [1]. One of these, the phase field approach, has been used to obtain a deeper understanding of the interfacial structure and its influence on the macroscopic phase boundary. It has also provided a unified framework for understanding a spectrum of (sharp) free boundary problems as limiting cases (see [2,3] and references therein). The chief difference between the sharp interface formulations and the phase field approach is that the former specifies the interface by means of conditions on the temperature (which is the only variable considered) while the latter uses a phase function as an independent variable which implicitly determines the interface location.

The simplest phase field model can be written as a system of parabolic equations for temperature $T(t, x)$ and phase or "order" parameter $\lambda(t, x)$ so that λ near 0 is one phase, e.g., solid, while λ near 1 is the other, e.g., liquid. An order parameter for a particular material or system is a variable which can be related to macroscopic observables and serves to distinguish the phases. In many areas of statistical mechanics it has also been related to microscopic quantities. In a system with complex dynamics, the order parameter is coupled to other variables, and is constrained to have a fixed value on each side of the equilibrium coexistence curve in the pressure-temperature plane. In this paper, we extend this development to include the effects of compressibility, mechanical and thermal heat transport, and different material properties in the two phases.

2. THE GENERAL MODEL

We first develop a very general system of equations before simplifying some aspects in order to facilitate analysis. We choose an arbitrary reference point on the coexistence curve between two phases (denoted by the subscript E) and we let $T^{(a)}$ and $P^{(a)}$ be the (absolute) temperature and pressure while $T \equiv T^{(a)} - T_E$ and $P \equiv P^{(a)} - P_E$ denote the temperature and pressure deviations. The other variables are the fluid velocity \vec{u} , the specific volume, w ($\equiv 1/\text{density}$), and the order parameter, λ . In the general case, we define a stress tensor, \vec{P} , which is coupled to the other variables. We use the standard notation $d/dt \equiv \partial/\partial t + \vec{u} \cdot \vec{\nabla}$ for the convective derivative.

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The equations governing such a system consist of conservation of mass, momentum, energy, an equation of state and a kinetic equation for the order parameter. Thus one has the continuity equation [4]

$$\frac{dw}{dt} = w \vec{\nabla} \cdot \vec{u}, \quad (2.1)$$

and Newton's law (neglecting gravitational forces),

$$\frac{d\vec{u}}{dt} = w \vec{\nabla} \cdot \vec{P} \quad \text{or} \quad \frac{du_j}{dt} = w \sum_i \frac{\partial}{\partial x_i} P_{ji}. \quad (2.2)$$

The heat balance equation is given by

$$(T + T_E) \frac{dS}{dt} = w \vec{\nabla} \cdot \vec{Q} \quad (2.3)$$

where S is entropy and \vec{Q} is the general heat flux vector (e.g., Fourier's law).

For any locally nonconserved order parameter, λ , the total time derivative of λ must balance the extent to which it is out of equilibrium. The latter is the λ variational derivative of the (Helmholtz) free energy \mathcal{F} . In terms of a rate constant A , one has the equation

$$\frac{d\lambda}{dt} = -A\mathcal{F}_\lambda. \quad (2.4)$$

where $\mathcal{F} = \int_\Omega F/w dx$. This is a generalization of the Landau-Ginzburg Model A formulation [5]. Analogously, one may also consider systems with conserved order parameters, corresponding to the Model B. An equation of state (obtained from the equilibrium properties) which is of the form

$$E(w, T^{(a)}, P^{(a)}, \lambda) = 0 \quad (2.5)$$

completes the general system of equations.

Thus, the system of equations (2.1)–(2.5) represent a complete, general model which can be studied upon specification of the form of E, \vec{P}, \vec{Q} and F . For further analysis, one must make suitable choices of these functions which are nevertheless sufficiently general to encompass a broad spectrum of materials.

3. THE DERIVATIONS

To proceed further, we consider a point (P_E, T_E) on the coexistence curve of the equilibrium phase diagram. Near this point, for which the specific volume has some value $w_E(\lambda)$, one may represent w in a series expansion in terms of T and P (the deviations from T_E and P_E) and neglect terms of order T^2, P^2 , so that

$$w(T, P, \lambda) = w_E(\lambda) + \varepsilon\eta(\lambda)T - \varepsilon^2\nu(\lambda)P \quad (3.1)$$

$$\varepsilon\eta \equiv \left. \frac{\partial w}{\partial T} \right|_{P, \lambda} = \text{coefficient of thermal expansion}$$

$$\varepsilon^2\nu \equiv - \left. \frac{\partial w}{\partial P} \right|_{T, \lambda} = \text{coefficient of isothermal compressibility} \quad (3.2)$$

We use the notation $\bar{w} \equiv \frac{1}{2}\{w_E(1) + w_E(0)\}$ and $[w]_E \equiv w_E(1) - w_E(0)$ and similarly for other variables where $w_E(1)$ denotes the specific volume at (P_E, T_E) in the liquid phase, etc. The simplest choices of the transition functions $w_E(\lambda), S_E(\lambda)$, and $\nu(\lambda)$ compatible with basic thermodynamic identities and inequalities are the linear functions

$$w_E(\lambda) \equiv \bar{w} + [w]_E \left(\lambda - \frac{1}{2} \right),$$

$$\begin{aligned} S_E(\lambda) &\equiv \bar{S} + [S]_E \left(\lambda - \frac{1}{2} \right), \\ \nu(\lambda) &\equiv \bar{\nu} + [\nu]_E \left(\lambda - \frac{1}{2} \right), \text{ etc.} \end{aligned} \quad (3.3)$$

Next, the free energy is assumed to be of the Landau-Ginzburg type with an additional term $q(T, w, \lambda)$ to incorporate the additional physics, so that

$$F = \frac{1}{2} \frac{D}{A} |\nabla \lambda|^2 + \frac{\alpha}{4} \lambda^2 (1 - \lambda)^2 + q(T, w, \lambda) \quad (3.4)$$

$$q(0, w_s, 0) = q(0, w_\ell, 1) = q_\lambda(0, w_s, 0) = q_\lambda(0, w_\ell, 1) = 0 \quad (3.5)$$

where $w_s = w_E(0)$, etc. There are two basic thermodynamic identities, namely,

$$-(P + P_E) = F_w \Big|_{T, \lambda} = q_w, \quad -S = F_T \Big|_{w, \lambda} = q_T \quad (3.6 \text{ a,b})$$

which are necessary for the compatibility of (3.1) and (3.4). By substituting (3.3) into (3.6a) and integrating, then performing the differentiation in (3.6b) using (3.4) one has upon utilizing the identity for the specific heat at constant volume, $C(\lambda)$,

$$C(\lambda) = (T + T_E) S_T \Big|_{w, \lambda}, \quad (3.7)$$

(neglecting variations of C in the pure phases) an expression for the $q(T, w, \lambda)$ term in the free energy, i.e.,

$$\begin{aligned} q &= \frac{1}{2\nu} \epsilon^{-2} (w - w_E)^2 - \left(P_E + \epsilon^{-1} \frac{\eta}{\nu} T \right) (w - w_E) \\ &\quad - C(\lambda) \{ (T + T_E) \ell n(1 + T/T_E) - T \} - S_E T + q_E(\lambda). \end{aligned} \quad (3.8)$$

If we now make the choice of Fourier law in the general heat balance equation (2.3) so that the right hand side is $w \vec{\nabla} \cdot K \vec{\nabla} T$ and use (3.8), (3.6b), (3.4) we obtain the heat equation

$$\begin{aligned} C(\lambda) \frac{dT}{dt} + \epsilon^{-1} \frac{\eta}{\nu} (T + T_E) w \vec{\nabla} \cdot \vec{u} + \{ C' \ell n(1 + T/T_E) + \epsilon^{-1} \left(\frac{\eta}{\nu} \right)' w \\ - \epsilon^{-1} (\eta \nu w_E)' + S'_E \} (T + T_E) \frac{d\lambda}{dt} = w \vec{\nabla} \cdot K \vec{\nabla} T. \end{aligned} \quad (3.9)$$

Note that the thermal conductivity K may depend on phase and temperature. The equation (3.9) is valid for an arbitrary choice of $w_E(\lambda)$, $S_E(\lambda)$, $C(\lambda)$, $\eta(\lambda)$, $\nu(\lambda)$. Letting $C_E \equiv C(\lambda)$ be a constant, and utilizing the thermodynamic identity

$$[S]_E [w]_E + P_E [\epsilon \eta]_E [w]_E - P_E [\epsilon^2 \nu]_E [S]_E = 0 \quad (3.10)$$

then implies to $O(1)$ in ϵ ,

$$\begin{aligned} C_E \frac{dT}{dt} + \epsilon^{-1} \frac{\eta}{\nu} (T + T_E) w \vec{\nabla} \cdot \vec{u} + \left\{ (\epsilon \nu)^{-1} \left([\eta]_E - \frac{\eta}{\nu} [\nu]_E \right) (w - \bar{w}) + [S]_E \right\} \\ (T + T_E) \frac{d\lambda}{dt} = w \vec{\nabla} \cdot K \vec{\nabla} T. \end{aligned} \quad (3.11)$$

Having derived the heat equation in a simple form, we now proceed to obtain a specific phase equation from (2.4) by deducing an appropriate formula for $q_E(\lambda)$. From the condition (3.5) and the condition

$$\frac{\partial}{\partial \lambda} \left\{ \frac{\alpha}{4} \lambda^2 (1 - \lambda)^2 + q \right\} \Big|_{w, T} = 0 \quad (3.12)$$

i.e., the equilibrium free energy (3.15) is at an extremum, one can obtain the set of conditions

$$q_E(0) = q_E(1) = 0 \quad q'_E(0) = q'_E(1) = -P_E[w]_E. \quad (3.13)$$

For simplicity, we let $q_E(\lambda)$ be the lowest degree polynomial consistent with the second order Taylor expansion of the Clausius-Clapeyron formula for the coexistence curve ($dP/dT = [S]/[w]$). We obtain from (3.13) the identity

$$q'_E(\lambda) = \frac{1}{2}P_E[w]_E \left\{ 1 - 12 \left(\lambda - \frac{1}{2} \right)^2 \right\} \quad (3.14)$$

Combining this expression with the remaining terms (3.8) and substituting into (3.4), (2.4), one obtains, upon discarding the $O(\epsilon)$ terms and using $B \equiv \epsilon A$, the phase equation

$$\frac{d\lambda}{dt} = \frac{B}{\epsilon} \left\{ \epsilon \frac{w}{B} \vec{\nabla} \cdot \frac{D}{w} \vec{\nabla} \lambda + \epsilon^{-1} \alpha \lambda (1 - \lambda) (\lambda - 1/2) + \frac{\eta}{\nu} \left([\eta]_E - \frac{1}{2} \frac{\eta}{\nu} [\nu]_E \right) T^2 + [S]_E T \right\} \quad (3.15)$$

A final simplification involves the stress tensor in (2.2). We replace P_{ij} with $-P^{(a)}\delta_{ij}$ to obtain the usual Euler's Equation

$$\frac{d\vec{u}}{dt} = -w \vec{\nabla} P. \quad (3.16)$$

Hence we obtain a complete system of equations in (2.1), (3.16), (3.1), (3.9), (3.11) in terms of the variables $(T, \lambda, \vec{u}, w, P)$, which can be studied subject to suitable initial and boundary conditions.

4. DISCUSSION AND CONCLUSIONS

The system of equations derived above offers two advantages. First, it treats the internal structure of the interface. Second, the equations are derived in a thermodynamically consistent manner. The latter point is especially important whenever one is using a set of macroscopic equations which are obtained from different sources. The imposition of interfacial conditions on \vec{u}, w, P would be especially tenuous in the absence of a complete theory. In fact, one can derive these conditions from the above equations via matched asymptotic analysis. In particular, one can generalize the classical Gibbs-Thomson relation $[S]_E T = -\sigma \kappa$, where σ is the surface tension and κ is the sum of the principal curvatures, which will be published elsewhere.

The integration of fluid properties with latent heat effects can be expected to play an important role in the study of dendritic sidebranching, particularly in light of experiments [6] which emphasize the role of convection in shape formation. It has been observed that the morphology of sidebranching, which occurs at the later stages of dendritic growth, is strongly influenced by the orientation of the experiments with respect to gravity, suggesting that the convection near the interface plays a fundamental role in the instabilities which govern these secondary spikes.

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