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Free Energy vs. Grand Potential Energy formulations in phase field modelling of alloy solidification

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Abstract.

We review and compare the [Wheeler-Boettinger-McFadden Phys. Rev A 45, 1992] (WBM), free energy based, phase field formulation of alloy solidification, with the grand potential energy formulation (GPF) of [Plapp Phys. Rev E 84 2011] and so, by association, the two phase approach of [Kim-Kim-Suzuki Phys. Rev. E 60 1999]. We ask what the effective differences are between these approaches: are they equivalent? We then advocate an approach that lies within the WBM scheme, yet remains consistent with the GPF. This has the flexibility to apply, with some modification, to arbitrary bulk free energies, including CALPHAD type descriptions such as Redlich-Kister relations for solution phases and sub-lattice models for non-stoichiometric intermetallics. The proposed model avoids some inherent complications implicit in the grand potential formulation, e.g. inverting the relation between chemical potential and solute concentration.

Introduction

The phase field modelling of binary alloy solidification involves the specification of a free energy functional, F, of the independent variables: phase ϕ , concentration c, and temperature T. Then, by specifying diffusion parameters the functional is optimally minimised to give the dynamic equations for ϕ, c and T. Within this framework, the modelling of any given material is centred on a description of the three diffusion parameters and the construction of the free energy functional, F.

Data bases such as CALPHAD [CALPHAD 2002] provide free energy densities of particular phases of matter as a function of c and T. Phase field modelling combines these bulk densities with the phase parameter to give the bulk free energy of the combined mixture, so that just as c provides the alloy concentration, ϕ provides the proportion of the two phases at any point in the domain.

In phase field the interface may be formally identified at the value of $\phi = 0.5$ intermediate between the bulk values, here solid at 0, and liquid at 1. To maintain a finite and slowly value of ϕ at the interface, a gradient $\nabla\phi$ and potential well are introduced, and in so doing can accommodate measured surface energy parameters.

This paper is concerned with bulk free energy construction rather than surface energy construction. Let us assume that we have two free energy densities for the two phases:

$$f_L = f_L(c,T), f_S = f_S(c,T). \tag{1}$$

A natural way to combine these densities into a bulk free energy density, f_B, using ϕ as a weight is:

$$f_B = f_B(\phi, c, T) = \phi\, f_L\,(c,T) + (1-\phi) f_S\,(c,T). \tag{2}$$

The driving force for phase change is then

$$\frac{\partial f_B}{\partial \phi} = f_L - f_S. \tag{3}$$

This is independent of ϕ and thus also, by implication, there is a force in the bulk. But we know that the driving force for phase change can only originate at the surface (the bulk is quite happy to remain in a metastable state). One way to address this issue is to introduce an interpolation function, $g(\phi)$ with gradients, $g'(\phi)$, that vanish at the extreme values $\phi = 0,1$, and write

$$f_B = g(\phi) f_L(c,T) + g(1-\phi) f_S(c,T), \tag{4}$$

where it is assumed $g(0) = 0, g(1) = 1$. A cubic function $g(\phi)$ is often chosen because it relates, a tanh shaped ϕ profile, $\phi = 1/2\left[1 + \tanh\left(\frac{x-Vt}{\delta}\right)\right]$, in 1D, by $V \propto \dot{\phi} \propto g'(\phi)(f_L - f_S)$. For pure metals $f_L - f_S \approx$ const, and at equilibrium, vanishes, but the WBM model does not have an analogous feature. This led M. Plapp and others to explore the use of the chemical potential, $\mu = \frac{\partial f}{\partial c}$ as a variable in order to define the bulk grand potential term

$$\omega_B = g(\phi)\omega_L(\mu, T) + g(1-\phi)\omega_S(\mu, T) \tag{5}$$

where $\omega_L(\mu_e, T) = \omega_S(\mu_e, T)$ for equilibrium chemical potential μ_e. If we now impose the property

$$\left.\frac{\partial \omega_B(\phi,\mu)}{\partial \phi}\right|_{\mu=\mu_e} = 0, \tag{6}$$

we have a model which resembles the pure metal,

$$\left.\frac{\partial f_B(\phi,\mu)}{\partial \phi}\right|_{T=T_e} = 0. \tag{7}$$

There is a major stumbling block with this approach: data bases do not routinely give energy densities in terms of chemical potential. However, this problem can easily overcome in situations where the free energy densities, f_L and f_S are quadratic in c, and indeed most if not all application of the grand potential formulation use quadratic approximation about the equilibrium concentrations of the true free energy densities.

The key to understanding the approach of [Plapp 2011] and co-workers is that, for each phase

$$\begin{aligned} \omega_L &= f_L - \mu_L c_L \\ \omega_S &= f_S - \mu_S c_S \end{aligned} \tag{8}$$

Where the chemical potentials are

$$\mu_L = \frac{\partial f_L(\,c_L, T)}{\partial c_L}, \mu_S = \frac{\partial f_S(\,c_S, T)}{\partial c_S}. \tag{9}$$

The new idea is to set

$$\mu_L = \mu_S, \tag{10}$$

and refer to this as *the* chemical potential, μ. These last equations allow us to find solutions, $c_L = c_L(\mu), c_S = c_S(\mu)$, and so allow us to write ω as a function of ϕ, μ and T. There is a subtlety here in that it appears, $\omega \neq f - \mu c$, the true Legendre transformation from f to ω. But we can, in principle, construct f from ω by using $f = \omega + \mu c$ to find the equivalent free energy construction. What we find is that the value of f intermediate between the pure phases interpolate (as a function of ϕ) in such a way as to have a common tangent throughout. If we can show, therefore, that the Legendre transformation from free energy to grand potential leaves the underlying system unchanged, it follows that using the approach of [Plapp 2011] is equivalent to a specific manner of interpolation of the pure phases.

The relation between Grand potential and Free energy formulation in phase field

Assume the free energy is a functional of ϕ, c

$$F = \int f(\phi, \nabla\phi, c)dV \tag{11}$$

and the grand potential is a functional of ψ, μ

$$\Omega = \int \omega(\psi, \nabla\psi, \mu)dV \tag{12}$$

The relation between the two potentials is given by

$$\omega = f - \mu c \tag{13}$$

where

$$\mu = \frac{\delta F}{\delta c}, c = -\frac{\delta \Omega}{\delta \mu}, \tag{14}$$

As a consequence the functionals are related

$$\Omega = F - \int \mu c \, dV \tag{15}$$

or

$$F = \Omega + \int \mu c \, dV \tag{16}$$

The transformation between the two potentials assumes that $\phi = \psi$, but we find it clearer to keep the notation for the phase distinct because

$$\left.\frac{\partial}{\partial\phi}\right|_c \neq \left.\frac{\partial}{\partial\psi}\right|_\mu \tag{17}$$

In fact

$$\begin{aligned}\frac{\partial}{\partial\phi} &= \frac{\partial\psi}{\partial\phi}\frac{\partial}{\partial\psi} + \frac{\partial\mu}{\partial\phi}\frac{\partial}{\partial\mu} \\ &= \frac{\partial}{\partial\psi} + \frac{\partial\mu}{\partial\phi}\frac{\partial}{\partial\mu}\end{aligned}$$

We also have

$$\frac{\partial}{\partial\nabla\phi} = \frac{\partial}{\partial\nabla\psi} + \frac{\partial\mu}{\partial\nabla\phi}\frac{\partial}{\partial\mu}, \tag{19}$$

Which implies

$$\begin{aligned}\frac{\delta\Omega}{\delta\phi} &= \frac{\partial\omega}{\partial\phi} - \nabla\cdot\frac{\partial\omega}{\partial\nabla\phi} \\ &= \left(\frac{\partial\omega}{\partial\psi} + \frac{\partial\mu}{\partial\phi}\frac{\partial\omega}{\partial\mu}\right) - \nabla\cdot\left(\frac{\partial\omega}{\partial\nabla\psi} + \frac{\partial\mu}{\partial\nabla\phi}\frac{\partial\omega}{\partial\nabla\mu}\right) \\ &= \frac{\partial\omega}{\partial\psi} - \nabla\cdot\frac{\partial\omega}{\partial\nabla\psi} + \frac{\partial\mu}{\partial\phi}\frac{\partial\omega}{\partial\mu} - \nabla\cdot\left(\frac{\partial\mu}{\partial\nabla\phi}\frac{\partial\omega}{\partial\mu}\right) \\ &= \frac{\delta\Omega}{\delta\psi} + \frac{\partial\mu}{\partial\phi}\frac{\partial\omega}{\partial\mu} - \nabla\cdot\left(\frac{\partial\mu}{\partial\nabla\phi}\frac{\partial\omega}{\partial\mu}\right).\end{aligned} \tag{20}$$

Applying this to Eq. (16) (in the second line below) gives

$$\begin{aligned}\frac{\delta F}{\delta\phi} &= \frac{\delta\Omega}{\delta\phi} + \frac{\delta\int\mu c}{\delta\phi} \\ &= \left(\frac{\delta\Omega}{\delta\psi} + \frac{\partial\mu}{\partial\psi}\frac{\partial\omega}{\partial\mu} - \nabla\cdot\left[\frac{\partial\mu}{\partial\nabla\phi}\frac{\partial\omega}{\partial\mu}\right]\right) + \frac{\delta\mu c}{\delta\phi} \\ &= \frac{\delta\Omega}{\delta\psi} + \frac{\partial\mu}{\partial\phi}\frac{\delta\Omega}{\delta\mu} - \nabla\cdot\left[\frac{\partial\mu}{\partial\nabla\phi}\frac{\delta\Omega}{\delta\mu}\right] + c\frac{\partial\mu}{\partial\phi} - \nabla\cdot c\frac{\partial\mu}{\partial\nabla\phi} \\ &= \frac{\delta\Omega}{\delta\psi} - \frac{\partial\mu}{\partial\phi}c + \nabla\cdot\left[\frac{\partial\mu}{\partial\nabla\phi}c\right] + c\frac{\partial\mu}{\partial\phi} - \nabla\cdot c\frac{\partial\mu}{\partial\nabla\phi} \\ &= \frac{\delta\Omega}{\delta\psi}\end{aligned} \tag{21}$$

where we have assumed no gradient of μ in ω (as is the case in [Plapp 2011]) so that

$$\frac{\delta\Omega}{\delta\mu} = \frac{\partial\omega}{\partial\mu} \tag{22}$$

We have allowed, though, that $\mu = \mu(\phi, \nabla\phi, c)$. The above calculation infers that

$$\dot{\phi} = -M\frac{\delta F}{\delta\phi} \tag{23}$$

is identical to

$$\dot{\psi} = -M\frac{\delta\Omega}{\delta\psi}, \tag{24}$$

since, clearly, $\dot{\phi} = \dot{\psi}$. If we can show that the equation for μ is indistinguishable from the standard equation for solute

$$\dot{c} = \nabla\cdot D\nabla\frac{\partial f}{\partial c}, \tag{25}$$

then we will have established that the GPF gives identical physics, and so an identical phase profile to WBM. This is achieved by using the chain rule

$$\dot{c} = \frac{\partial c}{\partial\psi}\dot{\psi} + \frac{\partial c}{\partial\mu}\dot{\mu} \tag{26}$$

plus Eq. (25). Since there is no freedom to choose the coefficients of $\dot{\psi}$ and $\dot{\phi}$ the resulting equation for μ must be equivalent to the equation for c. This might appear to counter the claim in Plapp 2011 that the equilibrium phase profile is different in the two formalisms. This paradoxical statement is resolved in the next section by a simple worked example.

The paradox resolved by example

We have seen that the GPF is formally identical to WBM, and yet clearly [Plapp 2011] claims that the two are different. The resolution of this is seen in the examples given in [Plapp 2011] where the chemical potential, $\boldsymbol{\mu}$ is not defined via $\boldsymbol{\mu} = \frac{\partial \boldsymbol{f}}{\partial \boldsymbol{c}}$ where $\boldsymbol{f}$ is defined as in WBM. The definition of $\boldsymbol{\mu}$ in [Plapp 2011] can be made compatible with $\boldsymbol{\mu} = \frac{\partial \boldsymbol{f}}{\partial \boldsymbol{c}}$ by changing the definition of $\boldsymbol{f}$. When this is done, we see that GPF is identical with WBM. Define example free energies

$$f_S = (c - 0.25)^2$$
$$f_L = (c - 0.75)^2 + 0.1c \qquad (27)$$

For our toy example we find using Eq. (8) that

$$\omega_L = 0.625 - c_L^2$$
$$\omega_S = 0.5625 - c_S^2 \qquad (28)$$

We can these to give two values of c

$$c_L = 0.25 + 0.5\mu$$
$$c_S = 0.7 + 0.5\mu. \qquad (29)$$

These are then inserted into Eqs. (28) as follows

$$\omega_L\big(c_L(\mu)\big) = 0.625 - c_L^2 = -0.25\mu - 0.25\mu^2$$
$$\omega_S\big(c_S(\mu)\big) = 0.5625 - c_S^2 = 0.0725 - 0.7\mu - 0.25\mu{\wedge}2 \qquad (30)$$

We can solve $\omega_L(c_L\mu)) = \omega_S(c_S\mu)$ to obtain, for example, the slope of the common tangent at equilibrium, $\mu_e = 0.16111$. The solute concentration is given by the relation Eq. (14) giving

$$c = 0.7 + 0.9\phi^3 - 1.25\phi^2 + 0.5\mu, \qquad (31)$$

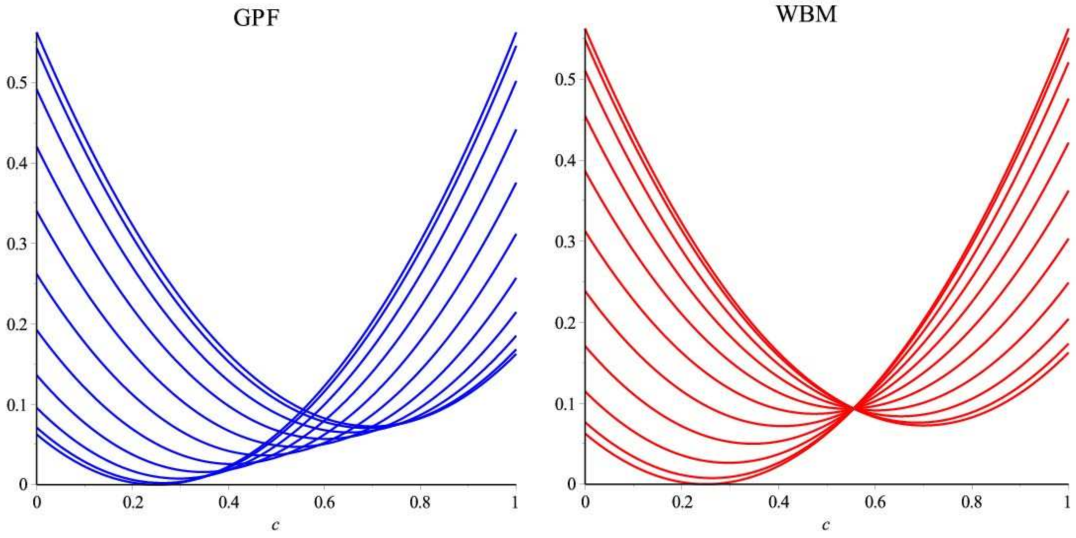
Which may be inverted to give

$$\mu = -1.8\phi^3 + 2.7\phi^2 - 1.4 + 2c. \qquad (32)$$

Now using the Legendre transformation, $f = \omega + \mu c$, we obtain

$$\mathrm{f} = .81\phi^6 - 2.43\phi^5 + 1.8225\phi^4 - 1.8\phi^3\,\mathrm{c}$$
$$+ 2.7\phi^2\mathrm{c} + \mathrm{c}^2 + 1.405\phi^3 - 2.1075\phi^2 + .5625 - 1.4\mathrm{c}. \qquad (33)$$

It is instructive to examine this as a series of 11 superimposed plots at fixed values of $\phi \in [0,1]$, shown below in blue, and to be compared with the equivalent WBM curves in red.



A direct approach to bulk free energy construction

We end with a more direct way of defining the free energy that is equivalent to the above, but more flexible. Define

$$f(\phi,c)=g(\phi)\bar{f}_L(\phi,c)+g(1-\phi)\bar{f}_S(\phi,c), \tag{34}$$

Where $g(\phi)=3\phi^2-2\phi^3$ and the barred functions are translations of f_L and f_S along the common tangent using ϕ:

$$\begin{aligned}\bar{f}_L(\phi,c)&=f_L[c-g(1-\phi)(c_S^e-c_L^e)]+g(1-\phi)([f_S(c_S^e)-f_L(c_L^e)],\\ \bar{f}_S(\phi,c)&=f_S[c-g(\phi)(c_L^e-c_S^e)]+g(\phi)[f_L(c_L^e)-f_S^e(c_S^e)].\end{aligned} \tag{35}$$

We find that the functional gradients are found to be

$$\begin{aligned}\frac{\partial f}{\partial c}&=gf_L'(c-g\Delta c+\Delta c)+(1-g)f_S'(c-g\Delta c)\\ \frac{\partial f}{\partial \phi}&=g'(f_L(c)-g\Delta c+\Delta c)-f_S(c-g\Delta c)-\Delta c\,\frac{\partial f}{\partial c}\end{aligned} \tag{36}$$

where $\Delta c=c_L^e-c_S^e$, and $c_L^e, c_S^e$are the equilibrium, common tangent values. These relations are, in principle, valid for any functions, f_L, f_S, and there is now no problem with function inversion. However, the data base functions f_L, f_S are not defined outside the interval $c\in[0,1]$ and so the above construction can only work if these functions can be extended outside this range, for example, by constructing a quadratic function about the equilibrium point with a common tangent and second derivative. A good alternative to this, which we have implemented, is to keep the data base functions, f_L, f_Sbetween c_L^e and $c_S^e$and extend as quadratic outside that range.

Conclusions

We have shown the equivalence of GPF and WBM phase field models, and that the apparent difference lies with free energy construction. GPF modelling inevitably involves compromise of the data base data in the metastable regions. Despite this, GPF modelling has many attractive features, which explains its adoption in many multiphase models, e.g. [Choudhury 2015],

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