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Bracket formalism applied to phase field models of alloy solidification

P.C. Bollada *, P.K. Jimack, A.M. Mullis

University of Leeds, United Kingdom

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ABSTRACT

We present a method for coupling current phase field models of alloy solidification into general continuum modelling. The advantages of this approach are to provide a generic framework for phase field modelling, give a natural and thermodynamically consistent extension to non-isothermal modelling, and to see phase field models in a wider context.

The bracket approach, introduced by Beris and Edwards, is an extension of the Poisson bracket of Hamiltonian mechanics to include dissipative phenomena. This paper demonstrates the working of this formalism for a variety of alloy solidification models including multi phase, multi species with thermal and density dependency.

We present new models by deriving temperature equations for single and more general phase field models, and give a density dependent formulation which couples phase field to flow.
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1. Introduction

The phenomena and process of alloy solidification, well described in [1], is now routinely associated with the significant successes of the modelling methods of phase field. Phase field came into being as a computational convenience (if not necessity) to capture the evolution of complex surface structures. More recently it has become possible to compute with physically realistic finite interface regions where the material is neither solid nor liquid, in which case the phase field becomes a physical field in the interface region.

Although it is well known that dissipative phenomena with constant boundary temperature spontaneously change to accommodate a lowering of the Gibbs free energy, the details of such transitions are still obscure for many complex materials. For dynamic modelling, this complexity is reflected in the construction of the Gibb's free energy, which typically includes both physical and non-physical states of matter – an example of the latter being the Gibbs free energy of a solid significantly above its melting temperature. Moreover, current computing resources and methods still struggle to grapple with the highly non-linear partial differential equations that the phase field method produces. Yet, in principle, the modelling of even complex materials using phase field is quite straightforward in outline: specify the global free energy of the physical system and allow the system to evolve spatially and temporally in such a way as to optimally minimise this functional in a thermodynamically consistent way. This manifests itself mathematically by the underlying presence of variational derivatives and diffusion parameters. To illustrate this, given a single phase formulation of the free energy, $F = \int_\Omega f(\phi, \nabla\phi, c, T)\,\mathrm{d}^3x$, in a domain Ω for the thermal-solutal (T, c) solidification of a metal, where $\phi \in [0, 1]$ indicates bulk melt or bulk solid at the extremes, the dynamical equations are typically given as, [2] a variational form for the phase variable

$$\dot{\phi} = -M\frac{\delta F}{\delta \phi}; \tag{1}$$

a conserved variational form for the solute concentration variable, c,

$$\dot{c} = \nabla \cdot D\nabla\frac{\delta F}{\delta c}; \tag{2}$$

and a temperature diffusion equation

$$C\dot{T} = \nabla \cdot \kappa\nabla T + L\dot{\phi}. \tag{3}$$

In the above M is phase mobility, D a solute diffusion parameter, κ thermal conductivity, C, and L are the volumetric heat capacity and volumetric latent heat parameters respectively - all prescribed. Also arising in the right hand side of Eq. (2) can be $\nabla \cdot \mathbf{j}$ where $\mathbf{j}$ is an anti-trapping current that compensates for non-physical effects in isothermal simulations associated with the computationally convenient use of a larger than realistic interface width, [3] – the anti-trapping current is not currently derived from a variational procedure and it is difficult to apply the mathematical analysis to general materials.There is likely to be a problem with a non -variational induced anti-trapping when applied to thermal models if the

* Corresponding author.
E-mail address: p.c.bollada@leeds.ac.uk (P.C. Bollada).

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current is not entropically neutral. Thus generation of an anti-trapping current from a variational procedure, if possible, which guarantees zero entropy generation may be advantageous. However, further discussion of this is beyond the scope of this paper.

The presence of $\nabla\phi$ in the free energy indicates a penalty in the free energy, i.e. an increase of free energy if the interface becomes too sharp. It is by no means obvious how three such different looking equations come from a single underlying principle. The form of these equations can be justified either by appeal to a sharp interface model, [4], or by assuming a finite interface and seeking thermodynamic consistency, [5].

This paper is concerned with the application of a generic non-equilibrium thermodynamic method to phase field modelling of alloy solidification. Multiphase models have been described without coupling to a temperature equation, for example by Nestler et al. [6] and, although it might be perfectly feasible to start from this formulation using the methods of, Penrose et al. [5], we are here applying the generic methods of Beris and Edwards [7]. Generic, in the sense that these methods apply to any continuum system with or without dissipative behaviour. Significant non-dissipative examples being: Euler flow and Elasticity; and dissipative examples being: Navier-Stokes, complex fluid modelling and visco-plasticity. This method has more in common with [5] than with [4], keeps the formal structure and the particular physical system concerned quite distinct, and brings to light differences and clarification when compared with other models (including single phase models) in the literature. The most obvious differences in the model are shown here to be in the temperature equation, which may be compared with single phase formulations as described in, [12–15].

The approach detailed here concerns a generalisation of the Poisson bracket for continuous non-dissipative phenomena and will be referred to as the "bracket" formalism. Application of the bracket produces a variational formulation, which in turn produces systems of coupled PDEs. In this sense there is a hierarchy:

Bracket → Variational form → PDEs.

Before embarking on a description of the bracket formalism as applied to phase field dynamics we state some reasons why this method may be preferable to other approaches, the main contender perhaps being the methods of Linear Irreversible Thermodynamics (LIT) [16]. The bracket formalism can be used to derive evolution equations for systems involving any number of coupled phenomena, and to guarantee that the couplings do not violate any principles of mechanics or laws of thermodynamics by construction. In LIT there is no provision for the inclusion of the kinematic of flow (as expressed by the Cauchy momentum equation) and the stress tensor. LIT provides expressions for the viscous or dissipative stresses, but cannot help with the conservative or elastic stresses. The bracket structure dictates the stress that appears in the Cauchy momentum equation, in terms of both conservative and dissipative contributions. Furthermore, these contributions are guaranteed to be mechanically and thermodynamically consistent between all of the coupled evolution equations necessary for the system description. In the bracket approach, the stress tensor field is given via a specification of the free energy functional, which is also something that does not come from LIT. In the phase field application here, we may wish to include flow modelling in a thermodynamically consistent way that will include conservative as well as dissipative phenomena. Indeed, the simple provision for an associated density change with phase already begins this coupling because conservation of mass implies the presence of flow. It is the generality of the bracket that is key here. The bracket formalism encompasses all continuous phenomena and provides a clear distinction between the conservative and dissipative contributions. In Section 7.1 of [7], the authors state their assumption that the Onsager/Casimir reciprocal relations are valid for systems close to equilibrium and that this implies that the lowest order representation of the dissipation bracket, as used here, must be a symmetric bilinear functional. Taking this as our starting point, we show, in agreement with [7], that the bracket formalism appears considerably easier to apply and perhaps less prone to error than other methods. Finally, even in the simplest phase field applications as explored in this paper, by applying the bracket in all generality there appear terms that have previously either been overlooked or neglected. Possibly the most important example of the latter is the correct construction of the temperature field equation.

The structure of the paper is as follows: Section 2 introduces the bracket and illustrates its application to a simple phase field model of solidification and then extends to include a thermal field. The temperature equations differ from the literature and so simulation results are presented which show the effect of the postulated new terms. Section 3 extends the bracket to apply to multi phase and multi species models of alloy solidification. Section 4 discusses previously neglected terms (postulated by a more general dissipative bracket) as providing additional enrichment for alloy modelling. Section 5 extends the single phase and multiphase model to include density. The key feature of this section is the introduction of the Poisson bracket alongside the dissipative bracket. The introduction of density implies a flow field so as to maintain mass conservation, an associated stress tensor, and additional terms to the pressure and temperature field.

The additional terms due to density modelling are easily extended to multiphase field formulations.

2. The bracket and phase field solidification

In this section we review the bracket and illustrate the formalism with single phase solidification modelling.

The bracket formalism is an extension of the Poisson bracket methodology of conservative, discrete particle systems to include dissipative and continuous systems. As is well known for conservative particle systems, dynamical equations are given once the Hamiltonian is prescribed in terms of the position and momentum. For example, for a single particle of mass m in a potential well V the Hamiltonian energy is given in terms of the momentum, $\mathbf{p}$ and position, $\mathbf{x}$ by

$$H(\mathbf{p},\mathbf{x}) = \frac{\mathbf{p}\cdot\mathbf{p}}{2m} + V(\mathbf{x}), \tag{4}$$

and the equations of motion for any variable, Q, by

$$\dot{Q} = \{Q, H\}. \tag{5}$$

In particular when Q represents the position and momentum of the particle:

$$\dot{x}_i = \{x_i, H\},$$

$$\dot{p}_i = \{p_i, H\}. \tag{6}$$

Here the Poisson bracket is specified by the antisymmetric operator (for arbitrary variables A, B)

$$\{A,B\} \equiv \sum_j^3 \left(\frac{\partial A}{\partial x_j}\frac{\partial B}{\partial p_j} - \frac{\partial A}{\partial p_j}\frac{\partial B}{\partial x_j} \right). \tag{7}$$

This gives as expected

$$\dot{x}_i = \frac{p_i}{m}, \tag{8}$$

$$\dot{p}_i = -\frac{\partial V}{\partial x_i}, \tag{9}$$

but also, for example, because of antisymmetry in the definition of Eq. (7),

$$\dot{H} = \{H, H\} = 0, \tag{10}$$

the conservation of energy. In moving from discrete particle systems to a continuum, the Hamiltonian energy function, being a summation of contributions from each particle, is extended by specifying a Hamiltonian energy functional and the discrete Poisson bracket has its continuous counterpart in an antisymmetric functional, see the final chapter Goldstein Classical Mechanics, [21] and also the review, [19]. Key applications of the continuous bracket are non-viscous flow and conservative elasticity. A major contribution of the authors in [7] has been to extend the continuous Poisson bracket in Chapter 5 to include continuous dissipative phenomena by the introduction of a dissipative bracket in Chapter 7. The dissipative bracket is similar to the Poisson bracket but with symmetric terms and the inclusion of a number of diffusion parameters. We illustrate the bracket approach using the well known phase field equations given in Eqs. (1) and (2).

Following [7] we: extend the Hamiltonian function of Eq. (4) with a specification of a free energy functional, F, of a set of n field variables, θ_i, $i \in [1, n]$; generalise the relations Eq. (5) to the functional relation

$$\dot{A} = [A, F], \tag{11}$$

where A is an arbitrary functional of θ_i, $i \in [1, n]$; and, finally, generalise the Poisson bracket of Eq. (7) by the specification of a dissipative bracket $[A, F]$. In its simplest form, this consists of the linear functional:

$$[A, F] = -\int_\Omega M_{ij} \frac{\delta A}{\delta \theta_i} \frac{\delta F}{\delta \theta_j} \, \mathrm{d}^3 x - \int_\Omega D_{ij} \nabla \frac{\delta A}{\delta \theta_i} \cdot \nabla \frac{\delta F}{\delta \theta_j} \, \mathrm{d}^3 x, \tag{12}$$

where summation is implied by repeated suffixes and Ω is a domain that we assume is large enough to exhibit natural boundary conditions. The matrices M_{ij} and D_{ij} are strictly positive definite in order that the system globally and optimally minimises F when used with Eq. (11). Indeed, we have, on replacing A with F, the relation,

$$\dot{F} = [F, F] < 0, \tag{13}$$

where the inequality replaces the equality of Eq. (10).

As a footnote to the above, multiphase fields, ϕ_i, are most conveniently given with a constraint, $\sum_{i=1}^{n} \phi_i = 1$, which leads to the diffusion matrices having a vanishing eigenvalue and, indeed, can have more than one. An example of the latter can be found in [8], which adopts a matrix first postulated in [11]. This is because, unlike single phase models, ϕ_i are not order parameters (see [8]). The implication here is that, for a set of true order parameters, θ_i. describing alloys, the matrices M_{ij} and D_{ij} are positive definite.

An example of modelling using non-conserved order parameters can be found in [9]. But there are examples, [10], which describe physical order parameters which, by definition sum to unity and so, by implication have a positive semi-definite dynamic matrix.

2.1. Bracket calculations for phase field alloys

A simple illustration of the bracket method is most easily achieved with an isothermal system of the two field variables, ϕ and c, where the dynamical equations follow from a specification of the free energy functional, $F[\phi, c]$, and the bracket

$$[A, F] \equiv -\int_\Omega M \frac{\delta A}{\delta \phi} \frac{\delta F}{\delta \phi} \, \mathrm{d}^3 x - \int_\Omega D \nabla \frac{\delta A}{\delta c} \cdot \nabla \frac{\delta F}{\delta c} \, \mathrm{d}^3 x. \tag{14}$$

This is a reduction of relation Eq. (12), where

$$\begin{pmatrix} \theta_1 \\ \theta_2 \end{pmatrix} = \begin{pmatrix} \phi \\ c \end{pmatrix}, \quad \mathbf{M} = \begin{pmatrix} M & 0 \\ 0 & 0 \end{pmatrix}, \quad \mathbf{D} = \begin{pmatrix} 0 & 0 \\ 0 & D \end{pmatrix}. \tag{15}$$

In Section 4 we consider more general models.

To make progress we require an extension of the chain rule to variational derivatives

$$\dot{A} = \int_\Omega \left(\frac{\delta A}{\delta \phi} \dot{\phi} + \frac{\delta A}{\delta c} \dot{c} \right) \mathrm{d}^3 x \tag{16}$$

and, by choosing the domain large enough so that variations of c and ϕ vanish on the boundary, we use integration by parts to give

$$-\int_\Omega D \nabla \frac{\delta A}{\delta c} \cdot \nabla \frac{\delta F}{\delta c} \, \mathrm{d}^3 x = \int_\Omega \frac{\delta A}{\delta c} \nabla \cdot D \nabla \frac{\delta F}{\delta c} \, \mathrm{d}^3 x. \tag{17}$$

Using Eqs. (11), (14), (16) and (17) and the arbitrariness of A allows us, by equating coefficients of $\frac{\delta A}{\delta \phi}$ and $\frac{\delta A}{\delta c}$, to recover the isothermal phase field equations Eqs. (1) and (2).

It should be noted that the specification of the bracket Eq. (14) is designed to return the given equations and in this sense is different to the Poisson bracket. In this case agreement with Eqs. (1) and (2) was achieved by the particular specification of the diffusion parameters, D and M in Eq. (12). The general guiding principles being that the bracket should be ideally (but not necessarily) linear in F, the coefficients M and D be positive, and the bracket should be *symmetric* in A and F. Following these principles leads to the more general bracket Eq. (12), which, as shown, includes Eq. (14) as a subset. There are, though, examples where the bracket includes antisymmetric terms [7]. These allow the possibility of including non-dissipative diffusive phenomena.

To include a temperature field, T, the free energy is specified as the functional, $F = F[\phi, c, T]$. However, it is more convenient to specify the bracket using an enthalpy functional, $E = E[\phi, c, s]$, where s is the entropy density, and use

$$\dot{A} = [A, E]. \tag{18}$$

in place of Eq. (11). For this extension the n variable bracket Eq. (12) (with $2n^2$ terms), is supplemented by terms linear in $\frac{\delta E}{\delta s}$ and $2(n+1)$ quadratic terms, which are prescribed once the linear terms are specified

$$\begin{aligned}[A, E] = &-\int_\Omega M_{ij} \frac{\delta A}{\delta \theta_i} \frac{\delta E}{\delta \theta_j} \, \mathrm{d}^3 x + \int_\Omega \frac{M_{ij}}{T} \frac{\delta A}{\delta s} \frac{\delta E}{\delta \theta_i} \frac{\delta E}{\delta \theta_j} \, \mathrm{d}^3 x \\ &- \int_\Omega D_{ij} \nabla \frac{\delta A}{\delta \theta_i} \cdot \nabla \frac{\delta E}{\delta \theta_j} \, \mathrm{d}^3 x + \int_\Omega \frac{D_{ij}}{T} \frac{\delta A}{\delta s} \nabla \frac{\delta E}{\delta \theta_i} \cdot \nabla \frac{\delta E}{\delta \theta_j} \, \mathrm{d}^3 x \end{aligned} \tag{19}$$

where, in the above, $\theta_{n+1} = s$. By, once again, neglecting off diagonal (cross) terms we produce the more manageable bracket for single phase binary alloy solidification:

$$\begin{aligned}[A, E] = &-\int_\Omega M \frac{\delta A}{\delta \phi} \frac{\delta E}{\delta \phi} \, \mathrm{d}^3 x + \int_\Omega \frac{M}{T} \frac{\delta A}{\delta s} \frac{\delta E}{\delta \phi} \frac{\delta E}{\delta \phi} \, \mathrm{d}^3 x - \int_\Omega D \nabla \frac{\delta A}{\delta c} \\ &\cdot \nabla \frac{\delta E}{\delta c} \, \mathrm{d}^3 x + \int_\Omega \frac{D}{T} \frac{\delta A}{\delta s} \nabla \frac{\delta E}{\delta c} \cdot \nabla \frac{\delta E}{\delta c} \, \mathrm{d}^3 x - \int_\Omega \frac{\kappa}{T} \nabla \frac{\delta A}{\delta s} \\ &\cdot \nabla \frac{\delta E}{\delta s} \, \mathrm{d}^3 x + \int_\Omega \frac{\kappa}{T^2} \frac{\delta A}{\delta s} \nabla \frac{\delta E}{\delta s} \cdot \nabla \frac{\delta E}{\delta s} \, \mathrm{d}^3 x. \end{aligned} \tag{20}$$

The reduction to Eq. (20) coming from the diffusion matrices specification:

$$\begin{pmatrix} \theta_1 \\ \theta_2 \\ \theta_3 \end{pmatrix} = \begin{pmatrix} \phi \\ c \\ s \end{pmatrix}, \quad \mathbf{M} = \begin{pmatrix} M & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \mathbf{D} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & D & 0 \\ 0 & 0 & \kappa/T \end{pmatrix}. \tag{21}$$

The bracket is written in terms of enthalpy, $E[\phi, c, s]$, rather than Gibbs free energy, $F[\phi, c, T]$, so that we can more easily specify the non-linear terms that guarantee the generation of entropy is

thermodynamically admissible, i.e. the three non-linear terms produce three strictly positive sources of entropy. This has the disadvantage, though, that the equation for the temperature field is derived less directly. In deriving the temperature equation we make use of generalised thermodynamic identities which bear an obvious resemblance to equilibrium identities.

The generalised thermodynamic potentials are related by

$$F = \int_\Omega f \,\mathrm{d}^3x = \int_\Omega (e - Ts)\,\mathrm{d}^3x = E - \int_\Omega Ts\,\mathrm{d}^3x, \tag{22}$$

where T is temperature and the enthalpy and free energy densities are respectively e and f. From Eq. (22), following the methods of [7], we can deduce the following generalised thermodynamic relations:

$$\left.\frac{\delta F}{\delta\phi}\right|_{c,T} = \left.\frac{\delta E}{\delta\phi}\right|_{c,s}, \quad \left.\frac{\delta F}{\delta c}\right|_{\phi,T} = \left.\frac{\delta E}{\delta c}\right|_{\phi,s}. \tag{23}$$

Eqs. (1) and (2) are recovered by using the chain rule for functionals

$$\dot{A} = \int_\Omega \left(\frac{\delta A}{\delta\phi}\dot{\phi} + \frac{\delta A}{\delta c}\dot{c} + \frac{\delta A}{\delta s}\dot{s}\right)\mathrm{d}^3x, \tag{24}$$

and matching coefficients of variational derivatives of the arbitrary functional, A, as before. We also derive an equation for entropy change by matching coefficients of $\frac{\delta A}{\delta s}$:

$$\dot{s} = \nabla\cdot\left(\frac{\kappa}{T}\nabla\frac{\delta E}{\delta s}\right) + \frac{M}{T}\frac{\delta E}{\delta\phi}\frac{\delta E}{\delta\phi} + \frac{\kappa}{T^2}\nabla\frac{\delta E}{\delta s}\cdot\nabla\frac{\delta E}{\delta s} + \frac{D}{T}\nabla\frac{\delta E}{\delta c}\cdot\nabla\frac{\delta E}{\delta c}. \tag{25}$$

To form an equation for T alone we require the generalised thermodynamic relations (also following the methods of [7])

$$T \equiv \left.\frac{\delta E}{\delta s}\right|_{c,\phi}, \quad s \equiv -\left.\frac{\delta F}{\delta T}\right|_{c,\phi}, \tag{26}$$

which together with Eq. (23) gives

$$\dot{s} + \nabla\cdot\mathbf{J}_s = \sigma, \tag{27}$$

where

$$\sigma = \frac{M}{T}\frac{\delta F}{\delta\phi}\frac{\delta F}{\delta\phi} + \frac{\kappa}{T^2}\nabla T\cdot\nabla T + \frac{D}{T}\nabla\frac{\delta F}{\delta c}\cdot\nabla\frac{\delta F}{\delta c}. \tag{28}$$

We see that there is a positive entropy source, σ and a flux, $\mathbf{J}_s = -\frac{\kappa}{T}\nabla T$. Thus the flow of s is seen to be thermodynamically admissible.

By assuming $s = -\frac{\delta F}{\delta T} = -\frac{\partial f}{\partial T}$ the chain rule for the entropy density variables in terms of ϕ, $\nabla\phi$, c and T is

$$\frac{\partial s}{\partial t} = \dot{\phi}\frac{\partial s}{\partial\phi} + \dot{c}\frac{\partial s}{\partial c} + \dot{T}\frac{\partial s}{\partial T}. \tag{29}$$

Using Eq. (27) in the new variables, along with Eq. (22), the phase equation Eq. (1) and solute equation Eq. (2), we derive, in Appendix A, the temperature equation:

$$C\dot{T} + \nabla\cdot\mathbf{q} = L\dot{\phi} + K\dot{c}. \tag{30}$$

Here

$$C(\phi,c,T) \equiv T\left.\frac{\partial s}{\partial T}\right|_{\phi,c}, \quad L(\phi,c,T) \equiv -\left.\frac{\delta E}{\delta\phi}\right|_{c,T},$$

$$K(\phi,c,T) \equiv -\left.\frac{\delta E}{\delta c}\right|_{\phi,T}, \tag{31}$$

where s given by Eq. (26), and the heat flux is given by,

$$\mathbf{q} \equiv -\kappa\nabla T - D\frac{\delta F}{\delta c}\nabla\frac{\delta F}{\delta c}. \tag{32}$$

C is the generalised heat capacity function. The generalised latent heat of fusion, L is related to the constant Latent heat, L_0 by

$$L_0 = \left|\int_0^1 L\,\mathrm{d}\phi\right|_{T_M} = E(T_M)_{\text{liquid}} - E(T_M)_{\text{solid}} \tag{33}$$

where we use the absolute value because the sign of L depends on the convention for the choice of $\phi = 0$ and $\phi = 1$. The use of L over L_0 allows for the value to change across the interface and also to change as the interface temperature varies. The interface temperature is usually not known in advance and therefore the use of L_0 is not strictly correct. Allowing latent heat to vary across the interface has been adopted by, for example, [2], but no authors to our knowledge implement dependence on temperature.

For practical computation, we use Eq. (26) to give

$$\frac{\partial s}{\partial c} = -\frac{\partial}{\partial c}\frac{\delta F}{\delta T}, \quad \frac{\partial s}{\partial T} \equiv -\frac{\partial}{\partial T}\frac{\delta F}{\delta T} \tag{34}$$

and Eq. (22) for the variational derivatives of enthalpy, E.

It is clear, in comparing Eq. (30) with Eq. (3), that there are terms neglected in the standard phase field treatment. Define

$$H_c \equiv \nabla\cdot D\frac{\delta F}{\delta c}\nabla\frac{\delta F}{\delta c} + K\dot{c} \tag{35}$$

and

$$H_\phi \equiv L\dot{\phi} \tag{36}$$

which gives on assuming s independent of $\nabla\phi$

$$C\dot{T} = \nabla\cdot\kappa\nabla T + H_\phi + H_c. \tag{37}$$

We conclude this subsection by observing that there are no free parameters in the temperature equation, once the bracket and free energy are specified: e.g. latent heat, L, is prescribed from the free energy functional, F; heat diffusivity, κ, from the bracket.

We look at the ratio of H_c to H_ϕ over the whole domain in the next subsection.

2.2. Example heating in Lead-Tin alloy

This section explores the significance of solute heating, H_c, as compared with heating associated with phase change, H_ϕ, using Pb-Sn alloy as an example. A convenient way of evaluating K is

$$K = -\left.\frac{\delta E}{\delta c}\right|_{\phi,T} = -\left(1 - T\frac{\partial}{\partial T}\right)\left.\frac{\partial f}{\partial c}\right|_{\phi,T}, \tag{38}$$

and similarly

$$L = -\left.\frac{\delta E}{\delta\phi}\right|_{c,T} = -\left(1 - T\frac{\partial}{\partial T}\right)\left.\frac{\delta F}{\delta\phi}\right|_{c,T}. \tag{39}$$

Note that the final term for L involves a variational derivative which includes gradients. Normally, in this term, we set $\frac{\delta F}{\delta\phi} = \frac{\partial f}{\partial\phi}$ and this omission is noted in [7], Chap. 10. However, we find that this term only plays a role in the initial transients and therefore is negligible for more steady simulations. For more details of the implementation see Appendix B.

We have a measure of the significance of H_c by inspecting the ratio

$$r = \frac{\int H_c\,\mathrm{d}^3x}{\int H_\phi\,\mathrm{d}^3x}. \tag{40}$$

at any moment in time. On inspection of the phase diagram for Pb-Sn, see Fig. 1, we expect the largest contribution from H_c when the partition coefficient, $k_E \equiv c_{\min}/c_{\max}$, local to the solidification interface, is far from unity. This is when the temperature approaches the eutectic temperature of 456 K. Using an initial

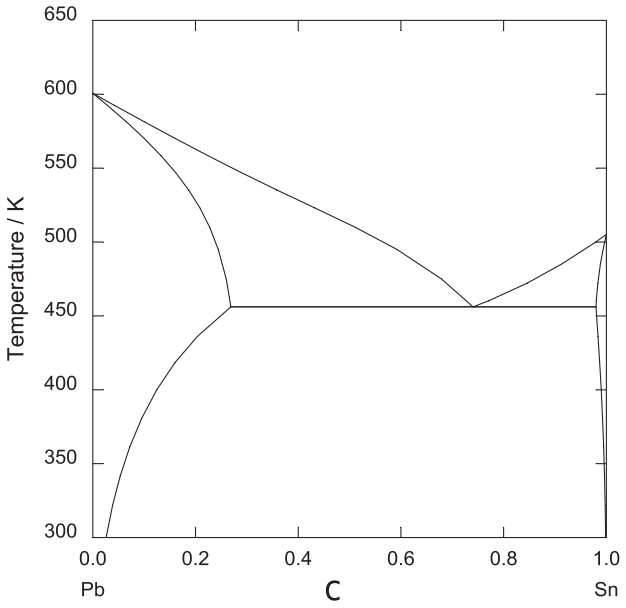

Fig. 1. Phase diagram for Pb-Sn.

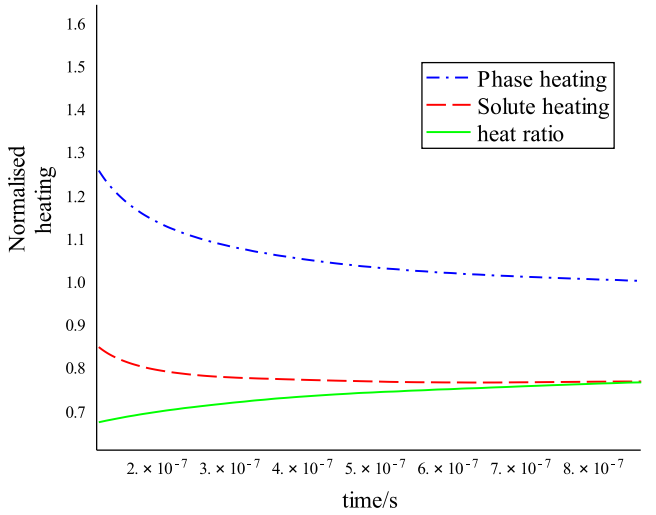

Fig. 2. Phase and solute heating for Pb-Sn alloy. The heating is normalised using the final phase heating value. The final ratio of solute to phase heating, $r \sim 0.77$.

condition of $c_0 = 0.4$ and $T = 475$ we find this ratio, at steady state, to be (see Fig. 2) of the order

$$r \sim 0.77, \tag{41}$$

indicating that solute heating is indispensable when there is substantial partitioning in the simulation. This result appears independent of interface width ($\delta = d_0, 2d_0$ and $4d_0$ were tried). However, for an initial condition of $c = 0.3$, implying a larger under cooling, the ratio, was reduced to $r \sim 0.2$ and so is less significant.

In conclusion, we find solute heating can be a vital ingredient for alloys with significant partitioning, but negligible for alloys where partitioning is small (e.g. Ni-Cu).

3. Multiphase and multi-species models

The power and significance of the bracket approach lies not only in offering an alternative formulation for deriving a thermodynamically consistent temperature equation, but also that it offers a straightforward method for generalising to more complex systems – namely multiphase and general alloy (multispecies) solidification with physically realistic expressions for free energy.

3.1. Multiphase models

Here we extend the bracket to multiphase binary alloys. Applying the summation rule from here on, and using the same simplification rule as in Eq. (20) the bracket becomes

$$[A,E] = -\int_\Omega M_{ab}\frac{\delta A}{\delta\phi_a}\frac{\delta E}{\delta\phi_b}\,\mathrm{d}^3x + \int_\Omega \frac{M_{ab}}{T}\frac{\delta A}{\delta s}\frac{\delta E}{\delta\phi_a}\frac{\delta E}{\delta\phi_b}\,\mathrm{d}^3x - \int_\Omega D\nabla\frac{\delta A}{\delta c}\cdot\nabla\frac{\delta E}{\delta c}\,\mathrm{d}^3x + \int_\Omega \frac{D}{T}\frac{\delta A}{\delta s}\nabla\frac{\delta E}{\delta c}\cdot\nabla\frac{\delta E}{\delta c}\,\mathrm{d}^3x, \; - \int_\Omega \frac{\kappa}{T}\nabla\frac{\delta A}{\delta s}\cdot\nabla\frac{\delta E}{\delta s}\,\mathrm{d}^3x + \int_\Omega \frac{\kappa}{T^2}\frac{\delta A}{\delta s}\nabla\frac{\delta E}{\delta s}\cdot\nabla\frac{\delta E}{\delta s}\,\mathrm{d}^3x, \tag{42}$$

and the chain rule becomes

$$\dot{A} = \int_\Omega \left(\frac{\delta A}{\delta\phi_a}\dot{\phi}_a + \frac{\delta A}{\delta c}\dot{c} + \frac{\delta A}{\delta s}\dot{s}\right)\mathrm{d}^3x, \tag{43}$$

from which

$$\dot{\phi}_a = -M_{ab}\frac{\delta F}{\delta\phi_b} \tag{44}$$

and the variational equation for c is as before, Eq. (2). The temperature equation generalises Eq. (30) to

$$C\dot{T} + \nabla\cdot\mathbf{q} = -\left.\frac{\delta E}{\delta\phi_a}\right|_{c,T}\dot{\phi}_a - \left.\frac{\delta E}{\delta c}\right|_{\phi,T}\dot{c} \tag{45}$$

where

$$\mathbf{q} \equiv -\kappa\nabla T - D\frac{\delta F}{\delta c}\nabla\frac{\delta F}{\delta c} \tag{46}$$

Note that the mobility has become tensorial, i.e. M_{ab}, in the multiphase formulation: this must be a symmetric semi positive definite matrix. The form of M_{ab} used by [6] is equivalent to a Lagrange multiplier times a scalar mobility, but other forms that preserve the connection with single phase and generalise to n-phase systems are proposed in [11].

3.2. Multi species alloys

Clearly this procedure easily extends to multi species alloys, e.g. ternary, where $\sum_a c_a = 1$. The result is very similar when $F = \int_\Omega f(\underline{\phi}, \nabla\underline{\phi}, \underline{c}, T)\,\mathrm{d}^3x$. That is, Eq. (44) together with solute concentration

$$\dot{c}_a = \nabla\cdot D_{ab}\nabla\frac{\delta F}{\delta c_b} \tag{47}$$

and temperature equation

$$C\dot{T} + \nabla\cdot\mathbf{q} = -\left.\frac{\delta E}{\delta\phi_a}\right|_{c,T}\dot{\phi}_a - \left.\frac{\delta E}{\delta c_a}\right|_{\phi,T}\dot{c}_a \tag{48}$$

where,

$$\mathbf{q} \equiv -\kappa \nabla T - D_{ab} \frac{\delta F}{\delta c_a} \nabla \frac{\delta F}{\delta c_b} \tag{49}$$

and D_{ab} has to take into account the constraint on c_a. For more general free energies in the form $F = \int_\Omega f(\underline{\phi}, \nabla \underline{\phi}, \underline{c}, \nabla \underline{c}, T)\, \mathrm{d}^3 x$ the variational forms above are unchanged.

4. New terms in single phase field models

The introduction of off diagonal (cross) terms in phase field is not new and has been explored, for example, by [20]. The model they advocate, in a notation close to ours for comparison, is

$$\dot{\phi} = -M_{11} \frac{\delta F}{\delta \phi} + M_{11} D_{12} \delta(\mathbf{J} \cdot \nabla \phi),$$

$$\dot{c} = \nabla \cdot \mathbf{J},$$

$$\mathbf{J} = D_{22} \left(\nabla \frac{\delta F}{\delta c} + D_{21} \delta \dot{\phi} \nabla \phi \right). \tag{50}$$

In [20] the authors adopt the Onsager symmetry relations to give $D_{12} = D_{21} > 0$. This model in turn may be brought back to the Karma model, [3], by setting $D_{12} = 0$ and replacing $\nabla \phi$ in the definition of $\mathbf{J}$, with the normal, $\nabla \phi / |\nabla \phi|$.

In order to more clearly explore the introduction of cross terms generated by the bracket formulation we return to the simpler isothermal system with bracket given by Eq. (12). The diffusion coefficients, D_{ij} are associated with Alan-Cahn like equations and the mobilities, M_{ij} with the Cahn-Hillard equations, so that we obtain

$$\dot{\theta}_i = -M_{ij} \frac{\delta F}{\delta \theta_j} + \nabla \cdot D_{ij} \nabla \frac{\delta F}{\delta \theta_j}. \tag{51}$$

By setting $i,j \in [1,2]$ and define $[\theta_1, \theta_2] = [\phi, c]$ we obtain

$$\begin{aligned} \dot{\phi} &= -M_{11} \frac{\delta F}{\delta \phi} - M_{12} \frac{\delta F}{\delta c} + \nabla \cdot D_{11} \nabla \frac{\delta F}{\delta \phi} + \nabla \cdot D_{12} \nabla \frac{\delta F}{\delta c} \\ \dot{c} &= -M_{21} \frac{\delta F}{\delta \phi} - M_{22} \frac{\delta F}{\delta c} + \nabla \cdot D_{21} \nabla \frac{\delta F}{\delta \phi} + \nabla \cdot D_{22} \nabla \frac{\delta F}{\delta c}. \end{aligned} \tag{52}$$

By observing that c is a conserved quantity we deduce that $M_{21} = M_{22} = 0$. Moreover, by assuming symmetry of M_{ij} we have $M_{12} = 0$. This leaves

$$\begin{aligned} \dot{\phi} &= -M_{11} \frac{\delta F}{\delta \phi} + \left\{ \nabla \cdot D_{11} \nabla \frac{\delta F}{\delta \phi} + \nabla \cdot D_{12} \nabla \frac{\delta F}{\delta c} \right\} \\ \dot{c} &= \nabla \cdot D_{22} \nabla \frac{\delta F}{\delta c} + \left\{ \nabla \cdot D_{21} \nabla \frac{\delta F}{\delta \phi} \right\} \end{aligned} \tag{53}$$

An exploration of the significance of the new coefficients (shown in curly brackets) will be postponed for future work. However, we do note here that although such extra terms can arise simply by a linear transformation of variables of a system with only diagonal contributions, the system in Eq. (53) cannot arise (see Appendix C). Thus the introduction of the new terms represents a possible enrichment of the current modelling approaches.

5. The full conservative-dissipative bracket

In this section we examine the methodology of the full bracket using an example. The full bracket is a sum of the dissipative bracket with the Poisson bracket for continuous systems (see the final chapter Goldstein Classical Mechanics, [21]). The necessity for introducing the full bracket comes about by the simple addition of density into the formulation. The equation for density change (mass conservation) is not dissipative and also involves flow, and, thus, we also require the correct equation for momentum change. Clearly there is coupling between the momentum equation and the other variables. We focus on pure metals for illustration and find, in line with other authors, that the stress tensor has a dependence on phase, and that partial time derivatives become convected derivatives.

5.1. Density dependent bracket

We begin with a free energy of the general form:

$$F = \int_\Omega f(\phi, \nabla \phi, c, T, \rho)\, \mathrm{d}^3 x. \tag{54}$$

For illustration purposes, we discuss here the simplest model that includes density variation due to change of phase.

The Poisson bracket for discrete particles as given in Eq. (7) is generalised to continua by

$$\{A, H\}_L = \int_\Omega \left[\frac{\delta A}{\delta \mathbf{x}} \cdot \frac{\delta H}{\delta \mathbf{p}} - \frac{\delta A}{\delta \mathbf{p}} \cdot \frac{\delta H}{\delta \mathbf{x}} \right] \mathrm{d}^3 X. \tag{55}$$

The subscript, L, here indicates that the coordinates, $\mathbf{X} \equiv [X, Y, Z]$ are Lagrangian, so that the Cartesian position, $\mathbf{x}$ is given as a function of the material coordinates, $\mathbf{X}$ and time, τ, i.e. $\mathbf{x} = \mathbf{x}(X, Y, Z, \tau), t = \tau$. The material coordinates, $\mathbf{X}$ are conventionally chosen to coincide with $\mathbf{x}$ at a given reference time, say $t = 0$, so that $\mathbf{x}(\mathbf{X}, \tau = 0) = \mathbf{X}$. Lagrangian coordinates are not convenient for fluid flow, however, and we seek a bracket more suitable for a Hamiltonian in Eulerian coordinates. In [7] chp. 5 the Hamiltonian for Euler flow is given by

$$H = \int_\Omega h(\mathbf{p}, \rho, s)\, \mathrm{d}^3 x = \int_\Omega \frac{\mathbf{p} \cdot \mathbf{p}}{2\rho} + e_p(\rho, \mathbf{x}, t) + u(\rho, s)\, \mathrm{d}^3 x. \tag{56}$$

Here ρ, s, e_p, u are mass, entropy, potential and energy densities respectively, and $\mathbf{p} = \rho \mathbf{u}$ is momentum density, where $\mathbf{u}$ is velocity. The potential energy, e_p, typically refers to gravitational potential. The internal energy, u, is the recoverable energy transfer associated with an idealised non-dissipative system and is related to volume changes and pressure, p, by

$$p = \rho \left. \frac{\partial u}{\partial \rho} \right|_s + s \left. \frac{\partial u}{\partial s} \right|_\rho - u. \tag{57}$$

The transition to the Eulerian form of Poisson bracket is not trivially derived from the Lagrangian form, Eq. (55). In [7] chp. 5 the authors use a 3 dimensional dirac delta function to move between Lagrangian and Eulerian integrals and give the Poisson bracket appropriate for the Hamiltonian of Eq. (56) as

$$\begin{aligned} \{A, H\}_E = &- \int_\Omega \left[\frac{\delta A}{\delta \rho} \nabla \cdot \left(\frac{\delta H}{\delta \mathbf{p}} \rho \right) - \frac{\delta H}{\delta \rho} \nabla \cdot \left(\frac{\delta A}{\delta \mathbf{p}} \rho \right) \right] \mathrm{d}^3 x \\ &- \int_\Omega \left[\frac{\delta A}{\delta s} \nabla \cdot \left(\frac{\delta H}{\delta \mathbf{p}} s \right) - \frac{\delta H}{\delta s} \nabla \cdot \left(\frac{\delta A}{\delta \mathbf{p}} s \right) \right] \mathrm{d}^3 x \\ &- \int_\Omega \left[\frac{\delta A}{\delta p_a} \nabla \cdot \left(\frac{\delta H}{\delta \mathbf{p}} p_a \right) - \frac{\delta H}{\delta p_a} \nabla \cdot \left(\frac{\delta A}{\delta \mathbf{p}} p_a \right) \right] \mathrm{d}^3 x. \end{aligned} \tag{58}$$

One feature of the Eulerian Poisson bracket not present in the Lagrangian form is the explicit dependence on the independent variables and the absence of the position as a variable.

Using H in Eq. (56) to give

$$\frac{\delta H}{\delta \mathbf{p}} = \frac{\mathbf{p}}{\rho} = \mathbf{u}, \tag{59}$$

$$\frac{\delta H}{\delta s} = \frac{\partial u}{\partial s}, \tag{60}$$

$$\frac{\delta H}{\delta \rho} = -\frac{\mathbf{p} \cdot \mathbf{p}}{2\rho^2} + \frac{\partial e_p}{\partial \rho} + \frac{\partial u}{\partial \rho}, \tag{61}$$

together with the chain rule

$$\dot{A} = \int_\Omega \left[\frac{\delta A}{\delta \mathbf{p}} \cdot \dot{\mathbf{p}} + \frac{\delta A}{\delta \rho} \dot{\rho} + \frac{\delta A}{\delta s} \dot{s} \right], \tag{62}$$

leads to the following ideal fluid equations: mass flow

$$\begin{aligned} \dot{\rho} &= -\nabla \left(\frac{\delta H}{\delta \mathbf{p}} \rho \right) \\ &= -\nabla \cdot (\rho \mathbf{u}), \end{aligned} \tag{63}$$

entropy flow

$$\begin{aligned} \dot{s} &= -\nabla \cdot \left(\frac{\delta H}{\delta \mathbf{p}} s \right) \\ &= -\nabla \cdot (s \mathbf{u}), \end{aligned} \tag{64}$$

and momentum flow

$$\dot{\mathbf{p}} = -\rho \nabla \frac{\delta H}{\delta \rho} - \nabla \cdot \left(\frac{\delta H}{\delta \mathbf{p}} \otimes \mathbf{p} \right) - \nabla \frac{\delta H}{\delta \mathbf{p}} \cdot \mathbf{p} - s \nabla \frac{\delta H}{\delta s} \tag{65}$$

or in components

$$\dot{p}_a = -\rho \frac{\partial}{\partial x_a} \frac{\delta H}{\delta \rho} - \frac{\partial}{\partial x_b} \left(\frac{\delta H}{\delta p_b} p_a \right) - p_b \frac{\partial}{\partial x_a} \frac{\delta H}{\delta p_b} - s \frac{\partial}{\partial x_a} \frac{\delta H}{\delta s}. \tag{66}$$

Using the equation for p in Eq. (57) and the mass equation, Eq. (63), it can be shown (see [7] Chap. 5) that the momentum equation is

$$\rho(\dot{\mathbf{u}} + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p - \rho \nabla e_p, \tag{67}$$

but we will drop the potential energy in the model from now on to focus on the fluid phase field interaction and write

$$\rho(\dot{\mathbf{u}} + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p. \tag{68}$$

We now wish to incorporate the phase variable into the Poisson bracket. Inspecting the methods of [7] for the density variables, ρ, s, $\mathbf{p}$ we can only apply this identically to the phase variable if we require ϕ to be a density and so vary under compression/expansion in a similar manner to s.

Our approach is to define an intermediate density variable, ρ_ϕ, use an identical approach in the Poisson bracket for entropy density, s, and then derive the phase field equations from the relationship between ρ_ϕ to ϕ. The phase field is then seen as a mass fraction. A similar approach is applied to solute concentration. Such phase densities obey their own conservation law (see [24] for further detailed discussion)

$$\dot{\rho}_\phi = -\nabla(\rho_\phi \mathbf{u}_\phi) \tag{69}$$

where $\mathbf{u}_\phi$ maybe thought of as the particle velocity of a particular phase and is only equal to the average velocity $\mathbf{u}$ in a small fluid element when there is no phase change.

We may define both the phase and solute variables by

$$\alpha^i = \frac{\rho^i_\alpha}{\rho}, \quad i = 1, 2, \ldots \tag{70}$$

where α is ϕ or c. For just two phases and species, we use the notation and relations:

$$\phi \equiv \phi^1 = \rho^1_\phi / \rho \equiv \rho_\phi / \rho \tag{71}$$

and

$$c \equiv c^1 = \rho^1_c \equiv \rho_c / \rho, \tag{72}$$

where ρ_ϕ is a phase density, and ρ_c is a concentration density. So it follows that the Poisson bracket for ρ_ϕ and ρ_c is, in analogy to s in Eq. (58)

$$\begin{aligned} \{A, H\}^{\phi,c}_E = &- \int_\Omega \left[\frac{\delta A}{\delta \rho_\phi} \nabla \cdot \left(\frac{\delta H}{\delta \mathbf{p}} \rho_\phi \right) - \frac{\delta H}{\delta \rho_\phi} \nabla \cdot \left(\frac{\delta A}{\delta \mathbf{p}} \rho_\phi \right) \right] \mathrm{d}^3 x \\ &- \int_\Omega \left[\frac{\delta A}{\delta \rho_c} \nabla \cdot \left(\frac{\delta H}{\delta \mathbf{p}} \rho_c \right) - \frac{\delta H}{\delta \rho_c} \nabla \cdot \left(\frac{\delta A}{\delta \mathbf{p}} \rho_c \right) \right] \mathrm{d}^3 x. \end{aligned} \tag{73}$$

With this additional contribution, in analogy with Eq. (64), the Poisson bracket alone produces equations:

$$\begin{aligned} \dot{\rho}_\phi &= -\nabla \cdot (\rho_\phi \mathbf{u}), \\ \dot{\rho}_c &= -\nabla \cdot (\rho_c \mathbf{u}). \end{aligned} \tag{74}$$

Note that, without any dissipation, both densities are conserved.

For a Hamiltonian consisting of only a kinetic term and isothermal free energy (as seen in Section 2, in models where temperature and entropy flow is of no importance the free energy, F, and the enthalpy, E, are interchangeable)

$$\begin{aligned} H[\rho, \mathbf{p}, \rho_\phi, \rho_c] &= \int_\Omega \frac{\mathbf{p} \cdot \mathbf{p}}{2\rho} \mathrm{d}^3 x + F \\ &= \int_\Omega \left[\frac{\mathbf{p} \cdot \mathbf{p}}{2\rho} + f(\rho_\phi, \nabla \rho_\phi, \rho_c, \rho) \right] \mathrm{d}^3 x. \end{aligned} \tag{75}$$

Here we work with free energy density, f, in place of internal energy, u, and [7] show that, for reversible systems, pressure is related more simply to the free energy:

$$p = \rho \frac{\partial f}{\partial \rho} - f, \tag{76}$$

which we expect to be modified by dissipative contributions. With the addition of the Poisson bracket, the full bracket is defined,

$$\begin{aligned} [\{A, H\}] &\equiv \{A, H\} + [A, H] \\ &= \{A, H\} + [A, F], \end{aligned} \tag{77}$$

where the slightly cumbersome notation for the full bracket used in [7] is also adopted here. It should be noted in the above that the dissipation does not contain any dissipative terms associated with mass density even though F is dependent on ρ.

The full bracket gives for the phase density

$$\begin{aligned} \dot{\rho}_\phi &= -\nabla \cdot (\rho_\phi \mathbf{u}) - \widetilde{M} \frac{\delta F}{\delta \rho_\phi} \\ \Rightarrow \frac{\mathrm{D}\rho_\phi}{\mathrm{D}t} &= -\rho_\phi \nabla \cdot \mathbf{u} - \widetilde{M} \frac{\delta F}{\delta \rho_\phi} \\ &= \frac{\rho_\phi}{\rho} \frac{\mathrm{D}\rho}{\mathrm{D}t} - \widetilde{M} \frac{\delta F}{\delta \rho_\phi} \\ \Rightarrow \rho \frac{\mathrm{D}(\rho_\phi / \rho)}{\mathrm{D}t} &= -\widetilde{M} \frac{\delta F}{\delta \rho_\phi}, \end{aligned} \tag{78}$$

where we used the following identity, for an arbitrary scalar or vector field, V

$$\frac{\mathrm{D}V}{\mathrm{D}t} \equiv \dot{V} + \mathbf{u} \cdot \nabla V. \tag{79}$$

and the mass conservation equation, Eq. (63), written in the form

$$\frac{\mathrm{D}\rho}{\mathrm{D}t} = -\rho \nabla \cdot \mathbf{u}. \tag{80}$$

One simple choice is $\widetilde{M} = \rho^2 M$, where M is the mobility for a constant density system. This choice, together with the chain rule

$$\frac{\delta}{\delta \rho_\phi} = \frac{\partial \phi}{\partial \rho_\phi} \frac{\delta}{\delta \phi} = \frac{1}{\rho} \frac{\delta}{\delta \phi}, \tag{81}$$

gives

$$\frac{\mathrm{D}\phi}{\mathrm{D}t} = -M \frac{\delta F}{\delta \phi}. \tag{82}$$

Now, the additional term to the right hand side of the momentum equation, Eq. (68), due to the contribution of phase density in the dissipative bracket, is

$$
\begin{aligned}
&-\rho_\phi \nabla \frac{\delta H}{\delta \rho_\phi} \\
&= -\rho_\phi \nabla \frac{\delta F}{\delta \rho_\phi} = -\nabla\left(\rho_\phi \frac{\delta F}{\delta \rho_\phi}\right) + \frac{\delta F}{\delta \rho_\phi}\nabla\rho_\phi \\
&= -\nabla\left(\rho_\phi \frac{\delta F}{\delta \rho_\phi}\right) + \left(\frac{\partial f}{\partial \rho_\phi} - \nabla\cdot\frac{\partial f}{\partial \nabla\rho_\phi}\right)\nabla\rho_\phi \\
&= -\nabla\left(\rho_\phi \frac{\delta F}{\delta \rho_\phi}\right) + \frac{\partial f}{\partial \rho_\phi}\nabla\rho_\phi + \frac{\partial f}{\partial \nabla\rho_\phi}\nabla\nabla\rho_\phi - \nabla\cdot\left(\frac{\partial f}{\partial \nabla\rho_\phi}\otimes\nabla\rho_\phi\right) \\
&= -\nabla\left(\rho_\phi \frac{\delta F}{\delta \rho_\phi}\right) + \nabla f - \nabla\cdot\left(\frac{\partial f}{\partial \nabla\rho_\phi}\otimes\nabla\rho_\phi\right) \\
&= -\nabla\left(\rho_\phi \frac{\delta F}{\delta \rho_\phi}\right) + \nabla f + \nabla\cdot\mathbf{T}, \qquad (83)
\end{aligned}
$$

where we used

$$
\nabla f(\rho_\phi, \nabla\rho_\phi) = \frac{\partial f}{\partial \rho_\phi}\nabla\rho_\phi + \frac{\partial f}{\partial \nabla\rho_\phi}\cdot\nabla\nabla\rho_\phi, \qquad (84)
$$

and defined

$$
\mathbf{T} = -\frac{\partial f}{\partial \nabla\rho_\phi}\otimes\nabla\rho_\phi. \qquad (85)
$$

This implies that the momentum equation Eq. (68) becomes

$$
\rho\frac{\mathrm{D}\mathbf{u}}{\mathrm{D}t} = -\nabla\left(\rho\frac{\partial f}{\partial \rho}\right) - \rho_\phi\nabla\frac{\delta F}{\delta \rho_\phi} = -\nabla p + \nabla\cdot\mathbf{T} \qquad (86)
$$

where the reversible pressure given in Eq. (76), is now modified to include dissipation, to

$$
p \equiv \rho\frac{\partial f}{\partial \rho} + \rho_\phi\frac{\delta F}{\delta \rho_\phi} - f. \qquad (87)
$$

Finally, we convert all the above to the phase variable, using the mapping

$$
\begin{aligned}
&\phi = \rho_\phi/\rho, \\
&\nabla\phi = \frac{\nabla\rho_\phi}{\rho} - \frac{\rho_\phi}{\rho^2}\nabla\rho, \qquad (88)
\end{aligned}
$$

and its inverse. Using the chain rules induced by the above, and that $f = f(\rho, \rho_\phi, \nabla\rho_\phi)$, i.e. the free energy includes no gradients of ρ, we have

$$
\begin{aligned}
p &= \rho\frac{\partial f}{\partial \rho}\bigg|_{\rho_\phi} + \rho_\phi\frac{\delta F}{\delta \rho_\phi} - f \\
&= \rho\frac{\delta F}{\delta \rho}\bigg|_{\rho_\phi} + \rho_\phi\frac{\delta F}{\delta \rho_\phi} - f \\
&= \left(\rho\frac{\delta F}{\delta \rho}\bigg|_{\phi} - \phi\frac{\delta F}{\delta \phi}\right) + \phi\frac{\delta F}{\delta \phi} - f \\
&= \rho\frac{\delta F}{\delta \rho}\bigg|_{\phi} - f, \qquad (89)
\end{aligned}
$$

which, assuming there is no gradient of density in the free energy, is

$$
p = \rho\frac{\partial f}{\partial \rho}\bigg|_{\phi} - f. \qquad (90)
$$

Note that the notation, $\frac{\partial f}{\partial \rho}\big|_{\rho_\phi}$ and $\frac{\partial f}{\partial \rho}\big|_{\phi}$ replaces the less precise, $\frac{\partial f}{\partial \rho}$, above where there is scope for ambiguity.

To obtain the stress we use the chain rule

$$
\frac{\partial}{\partial \nabla\rho_\phi} = \frac{1}{\rho}\frac{\partial}{\partial \nabla\phi} \qquad (91)
$$

and

$$
\nabla\rho_\phi = \rho\nabla\phi + \phi\nabla\rho, \qquad (92)
$$

to give

$$
\begin{aligned}
\mathbf{T} &= -\frac{\partial f}{\partial \nabla\rho_\phi}\otimes\nabla\rho_\phi \\
&= -\frac{\partial f}{\partial \nabla\phi}\otimes\nabla\phi + \frac{\phi}{\rho}\frac{\partial f}{\partial \nabla\phi}\otimes\nabla\rho. \qquad (93)
\end{aligned}
$$

Here the stress, in general, is not symmetric, but note that for an isotropic term in the free energy, with the gradient dependent term equal to $\frac{1}{2}\epsilon^2\nabla\phi\cdot\nabla\phi$, the stress tensor,

$$
\mathbf{T} = -\epsilon^2\nabla\phi\otimes\nabla\phi \ \text{(isotropic)}, \qquad (94)
$$

is symmetric. This result may be compared with the stress given without flow in [22] (but note the difference in sign). The bracket approach may be compared with the methods and results of [23]. However, in both these references the second term involving the effects of compressibility is absent. The irreversible isotropic stress component given in Eq. (94), can be compared with the reversible stress component for varying density in phase transitions between liquid and vapour system, proportional to $\nabla\rho\otimes\nabla\rho$. This classical reversible stress component has been known for more than a century, [17], and discussed in [18]

We pursue the equation for solute concentration, c, in a similar manner to that of ϕ (but without the complication of gradients, ∇c). Using a concentration density, $\rho_c(=\rho c)$ we find the Poisson bracket alone, in an identical way to entropy density, gives

$$
\dot{\rho}_c = -\nabla\cdot(\rho_c\mathbf{u}) \qquad (95)
$$

which can be written

$$
\frac{\mathrm{D}\rho_c}{\mathrm{D}t} = -\rho_c\nabla\cdot\mathbf{u}. \qquad (96)
$$

Adding the dissipative contribution modifies this to

$$
\frac{\mathrm{D}\rho_c}{\mathrm{D}t} = -\rho_c\nabla\cdot\mathbf{u} + \nabla\cdot\rho^2 D\nabla\frac{\partial f}{\partial \rho_c}, \qquad (97)
$$

where we have made explicit a density dependence in the solute diffusion to keep the physical dimensions consistent, and assumed no gradients of ρ_c in the free energy density. As with the phase equation, using the mass equation Eq. (63), allows us to rewrite this in terms of the order parameter, c, and thus, the solute equation of Eq. (2) is modified to

$$
\rho\frac{\mathrm{D}c}{\mathrm{D}t} = \nabla\cdot\rho^2 D\nabla\left(\frac{1}{\rho}\frac{\partial f}{\partial c}\right). \qquad (98)
$$

The coefficient D is decomposed into a diffusion term, α (units m^2/s), density ρ, the molar gas constant R, along with a reference molar volume, v_m and temperature, T_0, as

$$
D = \frac{\alpha}{\rho v_m R T_0} \qquad (99)
$$

The free energy density, f is assumed to have units $\mathrm{J/m}^3$. The values for the bulk free energies arising from a database are typically in units of J/mol which is readily converted to units of J/kg using molecular weights and/or the molar volume, v_m, of the species. Let us assume then that the natural free energy quantity from databases is $\hat{f}$ which has units of J/kg and assumed to have no dependence on density. Then using

$$
f = \rho\hat{f} \qquad (100)
$$

allows us to write

$$\rho \frac{\mathrm{D}c}{\mathrm{D}t} = \nabla \cdot \widetilde{D} \nabla \left(\frac{\partial \hat{f}}{\partial c} \right), \tag{101}$$

where

$$\widetilde{D} \equiv \frac{\rho \alpha}{v_m R T_0} = \rho^2 D. \tag{102}$$

The stress Eq. (93) and pressure Eq. (76) remain the same but with the modified free energy density, $f = f(\phi, \nabla\phi, \rho, c)$, meaning that pressure, in the momentum equation, will depend on the extra variable.

The above has a rather obvious extension to multiphase systems, where, for example, stress becomes

$$\mathbf{T} = -\frac{\partial f}{\partial \nabla \phi_a} \otimes \nabla \phi_a + \frac{\phi_a}{\rho} \frac{\partial f}{\partial \nabla \phi_a} \otimes \nabla \rho. \tag{103}$$

To extend the single phase case to include a temperature field we write the Hamiltonian, Eq. (75) as

$$\begin{aligned} H[\rho, \mathbf{p}, \phi, c, s] &= \int_\Omega \frac{\mathbf{p} \cdot \mathbf{p}}{2\rho} \mathrm{d}^3 x + E \\ &= \int_\Omega \left[\frac{\mathbf{p} \cdot \mathbf{p}}{2\rho} + e(\phi, \nabla\phi, \rho, s) \right] \mathrm{d}^3 x \end{aligned} \tag{104}$$

and extending the methods leading to the temperature equation, Eq. (30) in Section 2, to depend on ρ, we find from Eq. (64) that

$$\frac{\mathrm{D}s}{\mathrm{D}t} = -s \nabla \cdot \mathbf{u} \ = \frac{s}{\rho} \frac{\mathrm{D}\rho}{\mathrm{D}t}, \tag{105}$$

using Eq. (63), and the chain rule extends as

$$\frac{\mathrm{D}s}{\mathrm{D}t} = \frac{\partial s}{\partial \phi} \frac{\mathrm{D}\phi}{\mathrm{D}t} + \frac{\partial s}{\partial c} \frac{\mathrm{D}c}{\mathrm{D}t} + \frac{\partial s}{\partial \rho} \frac{\mathrm{D}\rho}{\mathrm{D}t}. \tag{106}$$

This results in material derivatives and an extra term due to the density, $J \frac{\mathrm{D}\rho}{\mathrm{D}t}$ in the temperature equation

$$C \frac{\mathrm{D}T}{\mathrm{D}t} = -\nabla \cdot \mathbf{q} + L \frac{\mathrm{D}\phi}{\mathrm{D}t} + K \frac{\mathrm{D}c}{\mathrm{D}t} + J \frac{\mathrm{D}\rho}{\mathrm{D}t} \tag{107}$$

where C, L, K, $\mathbf{q}$ are defined as before and the new term is taken from Eqs. (106) and (107) (on multiplying by T) to give

$$J \frac{\mathrm{D}\rho}{\mathrm{D}t} = \frac{sT}{\rho} \frac{\mathrm{D}\rho}{\mathrm{D}t} - T \frac{\partial s}{\partial \rho} \frac{\mathrm{D}\rho}{\mathrm{D}t}, \tag{108}$$

so that

$$J \equiv \left(\frac{1}{\rho} - \frac{\partial}{\partial \rho} \right) (sT) \tag{109}$$

where the thermodynamic identity for entropy is extended to

$$s \equiv -\frac{\delta F}{\delta T} = -\left. \frac{\partial f}{\partial T} \right|_{\rho, \phi, c}. \tag{110}$$

For multi-phase, multi-species systems, clearly the temperature equation of Eq. (48) is extended thus

$$C \frac{\mathrm{D}T}{\mathrm{D}t} + \nabla \cdot \mathbf{q} = L_a \frac{\mathrm{D}\phi_a}{\mathrm{D}t} + K_a \frac{\mathrm{D}c_a}{\mathrm{D}t} + J \frac{\mathrm{D}\rho}{\mathrm{D}t}, \tag{111}$$

where

$$L_a \equiv -\left. \frac{\delta E}{\delta \phi_a} \right|_{\rho, c, T, \phi_{b \neq a}}, K_a \equiv -\left. \frac{\delta E}{\delta c_a} \right|_{\rho, \phi_b, T, c_{b \neq a}}. \tag{112}$$

5.2. Free energy density construction

The purpose of this subsection is to suggest how to construct the free energy when density is included, i.e. how to extend from constant density models. The main assumption is that a data base will give free energy of each phase of matter in units of Joules per Mole. Since the free energy density is in Joules per volume the generalisation is primarily a matter of the correct placement of density and the number of moles per unit mass.

For simplicity we choose an isothermal single phase binary alloy with free energy functional:

$$F = \int_\Omega f(\phi, \nabla\phi, c, \rho) \mathrm{d}^3 x \tag{113}$$

where the free energy density is given in terms of its surface and volume components by

$$f = f^S(\nabla\phi) + f^V(\phi, c, \rho). \tag{114}$$

For anisotropic solidification we have

$$f^S = \frac{1}{2} |\epsilon A(\nabla\phi) \nabla\phi|^2 \tag{115}$$

where ϵ is a constant surface energy term and, for example, a cubic symmetry is incorporated by

$$A(\nabla\phi) \equiv 1 - 3a + 4a(n_x^4 + n_y^4)/|\mathbf{n}|^4, \quad \mathbf{n} \equiv \frac{\nabla\phi}{|\nabla\phi|}, \tag{116}$$

where a governs the strength of anisotropy (e.g. $a \sim 0.02$ see [26]). The volume term is given by

$$f^V = \rho \left[g(\phi) f^V_{\mathrm{sol}}(c, T) + g(1-\phi) f^V_{\mathrm{liq}(c,T)} \right] \tag{117}$$

where T is the isothermal temperature,

$$f^V_i = v(c) f^V_{i,\mathrm{mol}}, \tag{118}$$

with

$$v(c) \equiv (1-c) v^A + c v^B, \tag{119}$$

and v^A being the moles per mass of each alloy species.

With this definition of the free energy the governing equations are given by

$$\frac{\mathrm{D}\phi}{\mathrm{D}t} = -M(c) \frac{\delta F}{\delta \phi}, \tag{120}$$

where the mobility is given by

$$M(c) \equiv (1-c) M^A + c M^B. \tag{121}$$

The solute equation is (see previous subsection for definition of $\widetilde{D}$ and $\hat{f}$)

$$\rho \frac{\mathrm{D}c}{\mathrm{D}t} = \nabla \cdot \widetilde{D}(\phi, c, \rho) \nabla \frac{\partial \hat{f}}{\partial c}, \tag{122}$$

where

$$\widetilde{D}(\phi, c, \phi) = \frac{\rho \left[\phi D_{\mathrm{sol}} + (1-\phi) D_{\mathrm{liq}} \right] c(1-c)}{R T_0 v(c)}, \tag{123}$$

$D_{\mathrm{sol}} \ll D_{\mathrm{liq}}$ are the solute diffusion constants and R is the molar gas constant.

Mass continuity is

$$\dot{\rho} = -\nabla \cdot (\rho \mathbf{u}), \tag{124}$$

and momentum continuity by

$$\rho \frac{\mathrm{D}\mathbf{u}}{\mathrm{D}t} = -\nabla p + \nabla \cdot \mathbf{T} \tag{125}$$

where pressure is given by

$$p = \rho \frac{\partial f}{\partial \rho} - f = -f^S(\nabla\phi) = -\frac{1}{2} |\epsilon A \nabla\phi|^2 \tag{126}$$

and stress by

$$\mathbf{T} \equiv -\frac{\partial f}{\partial \nabla\phi} \otimes \nabla\phi + \frac{\phi}{\rho}\frac{\partial f}{\partial \nabla\phi} \otimes \nabla\rho, \tag{127}$$

where

$$\frac{\partial f}{\partial \nabla\phi} = \frac{\partial f^S}{\partial \nabla\phi} = \epsilon^2 A^2 \nabla\phi + \epsilon^2 A |\nabla\phi|^2 \frac{\partial A}{\partial \nabla\phi}. \tag{128}$$

It is to be expected in most situations that $|\nabla\rho/\rho| \ll |\nabla\phi|$ and so the second term in stress may legitimately dropped. Using the notation $\nabla\phi \equiv [\phi_{,1}, \phi_{,2}, \phi_{,3}]^T$ and

$$\frac{\partial A}{\partial \nabla\phi} \equiv \left[\frac{\partial A}{\partial \phi_{,1}}, \frac{\partial A}{\partial \phi_{,2}}, \frac{\partial A}{\partial \phi_{,3}}\right]^T, \tag{129}$$

it can be shown (see [26]) for explanation and also divergence of this term that

$$\frac{\partial A}{\partial \phi_{,i}} = \frac{4\phi_{,i}}{|\nabla\phi|^2}\left(4a\frac{\phi_{,i}^2}{|\nabla\phi|^2} - A + 1 - 3a\right). \tag{130}$$

6. Conclusions

We have presented the bracket formulation in the context of the phase field method in alloy solidification. Its main use being the ability to build phase field models in all generality whilst keeping the thermodynamics consistent. We have illustrated the procedure beginning with the simplest models of alloy solidification and then extending to modelling non-isothermal, multi-phase and multi-solute materials. Density dependence introduces reversible (non-dissipative) behaviour into the system and the bracket provides a comprehensive framework for this coupling. Clearly the formalism applies to more complicated models such as complex fluids with phase change.

The key advantages of using the bracket approach can be summarised:

- Natural extension to non-isothermal models.
- Provides a general framework for phase field modelling.
- The opportunity to add more generality to phase field modelling.

and the specific contributions of this paper are to:

- Produce a thermodynamically correct temperature equation for single and multi phase models and density dependent models.
- Highlight the importance of solute heating in the temperature equation, providing one example where this heating is essential and thereby suggesting that this term is probably significant in all but the simplest materials.
- Write down the equations for phase field modelling when density is included. This provides a model for when density varies between phases and will have its key application in 3 dimensions where buoyancy is of major concern.

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Appendix A. Mathematical derivation of Eq. (30)

Beginning with Eq. (25) multiplying by T gives

$$\begin{aligned} T\dot{s} &= T\nabla\cdot\left(\frac{\kappa}{T}\nabla\frac{\delta E}{\delta s}\right) + M\frac{\delta E}{\delta\phi}\frac{\delta E}{\delta\phi} + \frac{\kappa}{T}\nabla\frac{\delta E}{\delta s}\cdot\nabla\frac{\delta E}{\delta s} + D\nabla\frac{\delta E}{\delta c}\cdot\nabla\frac{\delta E}{\delta c} \\ &= \nabla\cdot\left(\kappa\nabla\frac{\delta E}{\delta s}\right) - \frac{\kappa}{T}\nabla T\cdot\nabla\frac{\delta E}{\delta s} + M\frac{\delta E}{\delta\phi}\frac{\delta E}{\delta\phi} + \frac{\kappa}{T}\nabla\frac{\delta E}{\delta s}\cdot\nabla\frac{\delta E}{\delta s} + D\nabla\frac{\delta E}{\delta c}\cdot\nabla\frac{\delta E}{\delta c} \\ &= \nabla\cdot\kappa\nabla T + M\frac{\delta E}{\delta\phi}\frac{\delta E}{\delta\phi} + D\nabla\frac{\delta E}{\delta c}\cdot\nabla\frac{\delta E}{\delta c}, \end{aligned} \tag{131}$$

where the last simplification came from using the first relation from Eq. (26) to cancel terms.

We now use Eqs. (1) and (23) to write

$$M\frac{\delta E}{\delta\phi}\Big|_{s,c}\frac{\delta E}{\delta\phi}\Big|_{s,c} = M\frac{\delta F}{\delta\phi}\Big|_{T,c}\frac{\delta F}{\delta\phi}\Big|_{T,c} = -\dot{\phi}\frac{\delta F}{\delta\phi}\Big|_{T,c}. \tag{132}$$

Similarly we use Eqs. (2) and (23) to rewrite

$$\begin{aligned} D\nabla\frac{\delta E}{\delta c}\Big|_{\phi,s}\cdot\nabla\frac{\delta E}{\delta c}\Big|_{\phi,s} &= \nabla\frac{\delta F}{\delta c}\Big|_{\phi,T}\cdot D\nabla\frac{\delta F}{\delta c}\Big|_{\phi,T} \\ &= \nabla\cdot D\frac{\delta F}{\delta c}\nabla\frac{\delta F}{\delta c} - \frac{\delta F}{\delta c}\nabla\cdot D\nabla\frac{\delta F}{\delta c} \\ &= \nabla\cdot D\frac{\delta F}{\delta c}\nabla\frac{\delta F}{\delta c} - \frac{\delta F}{\delta c}\dot{c}. \end{aligned} \tag{133}$$

Now, the relations coming from Eq. (22) imply

$$\frac{\delta F}{\delta c} = \frac{\delta E}{\delta c} - T\frac{\partial s}{\partial c}, \tag{134}$$

$$\frac{\delta F}{\delta \phi} = \frac{\delta E}{\delta \phi} - T\frac{\partial s}{\partial \phi}, \tag{135}$$

(all in the T, c, ϕ space) and the chain rule, Eq. (29), for s is

$$T\dot{s} = T\frac{\partial s}{\partial\phi}\dot{\phi} + T\frac{\partial s}{\partial c}\dot{c} + T\frac{\partial s}{\partial T}\dot{T}. \tag{136}$$

So that starting from Eq. (131) together with Eqs. (132) and (133), we collect terms in $\dot{\phi}$ and $\dot{c}$ on the right hand side, and apply Eqs. (134) and (135). For example, collecting terms in $\dot{\phi}$ gives

$$\left(-T\frac{\partial s}{\partial\phi} - \frac{\delta F}{\delta\phi}\right)\dot{\phi} = -\frac{\delta E}{\delta\phi}\dot{\phi} \tag{137}$$

and similarly in $\dot{c}$. Finally, using the definitions Eq. (31) and the heat flux relation, Eq. (32) we obtain the heat equation Eq. (30).

Appendix B. Detail of the Pb-Sn model

In our simulations, using an implementation based on [26] we used slightly modified parameters from the isothermal model of [25] in our thermal model (for Lead (A), tin(B)): Mobility (m^3/J)

$$M^A = \frac{T^A\mu^A}{6\sqrt{2}L^A\delta^A}, \quad M^B = \frac{T^A\mu^B}{6\sqrt{2}L^B\delta^B}. \tag{138}$$

For surface energy (J/m) we take

$$\epsilon^A = 6\sqrt{2}\sigma^A\delta^A, \quad \epsilon^B = 6\sqrt{2}\sigma^B\delta^B \tag{139}$$

and energy barrier (J/m^3) in the double well potential

$$W^A = \frac{3\sigma^A}{\sqrt{2}\delta^A}, \quad W^A = \frac{3\sigma^B T^A}{\sqrt{2}\delta^B T^B}. \tag{140}$$

Solute diffusion is given by

$$D = \frac{\phi D_c^{\mathrm{sol}} + (1-\phi) D_c^{\mathrm{liq}}}{RT_0} \tag{141}$$

where we assume the free energy is in J/mol for the solute equation and convert to J/m^3 for the phase field equation using $v = (1 - cv^A + cv^B$.

It remains to specify the free energy density,

$$f = \frac{1}{2}\epsilon|A(\nabla\phi)\nabla\phi|^2 + W\phi_2(1-\phi)^2 + g(\phi)f_{\mathrm{liq}} + (1-g(\phi))f_{\mathrm{sol}} \tag{142}$$

where using $i = \mathrm{liq}, \mathrm{sol}$,

$$f_i = (1-c)h_i^A(T) + ch_i^B(T) + h_i^{\mathrm{RK}}(c,T). \tag{143}$$

The Gibbs expansions are

$$h_i^{A(B)} = \sum_{j=1}^{8} h_{ij}^{A(B)} T_j, \tag{144}$$

where

$$T_{j=1,8} = [1, T, T\ln T, T^2, T^3, 1/T, T^7, 1/T^9]. \tag{145}$$

The Redlich-Kister terms are

$$h_i^{\mathrm{RK}}(c,T) = (h_{ij}^a + Th_{ij}^b)K_j(c) \tag{146}$$

where

$$K_j = \begin{cases} c(1-c) & j = 1 \\ (1-2c)K_{j-1} & j > 1. \end{cases} \tag{147}$$

We will not give the thermodynamic coefficients, h_i^A, h_i^B, h_{ij}^a and h_{ij}^b, which can be found in a data base such as MTDATA, [27], which also gives the phase diagram shown in Fig. 1. Table 1 provides information and parameters used in the simulation. We remind the reader that the aim of this simulation is to indicate the relevance of solute heating in general, not to give a physically accurate simulation of Pb-Sn solidification *per se*. Nonetheless, we choose physically realistic values where possible. The choice of the very small value for interface width, $\delta \sim 2d_0$ allows a reasonably realistic kinetic coefficient, $\mu \sim 0.4$ m/(Ks), which is slightly lower than, say, [2] $\mu \sim 2$ m/(Ks), but, inline with [25], is still expedient for computation. The Lewis number, $Le = 100$, in particular, is far less than physically realistic, $Le = 10,000$, but we judge the value used to be high enough to judge the significance of the relative strength of the heating sources. The mesh size, though insufficient for very accurate measurement of, say, tip velocity and radius, appears sufficient to resolve the solute field and demonstrate the significance of solute heating. The value initial solute value of $c_0 = 0.4$ together with $T = 475$ K were chosen to maximise the solute heating effect. Characteristic values are chosen for computational reasons, the surface energy comes from [28] and others are typical in the literature, e.g. [25].

Table 1
Table of parameters used in our simulation for demonstrating the significance of solute heating in Lead-Tin solidification.

Parameter	Variable	Value
Molar gas constant	R	8.31 m^2 kg/s^2/K/mol
Boundary temp	T_0	475 K
Lead melting temp	T_A	600 K
Tin melting temp.	T_B	505 K
Boundary and initial solute	c_0	0.4
Characteristic time	τ	0.03293 ns
Characteristic speed	v	0.03293 ns
Characteristic length	L	1 nm
Characteristic diffusivity	α	0.30366×10^{-7} m^2/s
Diffusivity liquid	D_c^{liq}	10^{-9} m^2/s
Diffusivity solid	D_c^{sol}	10^{-13} m^2/s
Lewis number	$Le \equiv \kappa/D_c^1$	100
Anisotropy	a	0.02
Kinetic coefficient Pb and Sn	$\mu^A(\mu^B)$	0.4 m/(Ks)
Surface energy-Pb(Sn)	$\sigma^A(\sigma^B)$	0.033(0.059) J/m^2
Initial radius	ρ_0	10 L
Domain size		1000 L $\times$ 1000 L
Mesh size	Δx	0.78 L
Time step	Δt	0.5τ
Capillary length	d_0	0.5 nm
Interface width Pb	δ^A	$2d_0$
Interface width Sn	δ^B	$\delta^A(T_B/T_A)(\sigma^A/\sigma^B)$
Latent heat	$L^A(L^B)$	$2.6(4.3) \times 10^8$ J/m^3
Moles per vol	$v_A(v^B)$	54,730(61,505) mol/m^3

Appendix C. Cross terms due to linear transformation

We wish to explore the possibility that a linear transformation between the phase variable, $\phi \in [0,1]$, and the conserved solute variable, $c \in [0,1]$ to new variables, say w_1 and w_2, leads to cross terms if the transformed variables, w_i, have the same properties, $w_1, w_2 \in [0,1]$ with w_2 conserved.

Writing $v_1 = \phi$, $v_2 = c$, we begin with the general isothermal model

$$\dot{v}_a = -M_{ab}\frac{\delta F}{\delta v_b} + \nabla \cdot D_{ab}\nabla\frac{\delta F}{\delta v^b}, \tag{148}$$

which we may write in matrix notation as

$$\dot{\mathbf{v}} = -\mathbf{M}\frac{\delta F}{\delta \mathbf{v}} + \nabla \cdot \mathbf{D}\nabla\frac{\delta F}{\delta \mathbf{v}}. \tag{149}$$

The familiar isothermal solute model with only diagonal terms is returned on setting

$$\mathbf{M} = \begin{bmatrix} M & 0 \\ 0 & 0 \end{bmatrix}, \quad \mathbf{D} = \begin{bmatrix} 0 & 0 \\ 0 & D \end{bmatrix}. \tag{150}$$

Now consider a symmetric linear transformation

$$\mathbf{w} = \mathbf{A}\mathbf{v}. \tag{151}$$

Then upon substitution of Eq. (151) into (149) gives

$$\mathbf{A}^{-1}\dot{\mathbf{w}} = -\mathbf{M}\mathbf{A}\frac{\delta F}{\delta \mathbf{w}} + \nabla \cdot \mathbf{D}\mathbf{A}\nabla\frac{\delta F}{\delta \mathbf{w}}, \tag{152}$$

so that

$$\dot{\mathbf{w}} = -\mathbf{N}\frac{\delta F}{\delta \mathbf{w}} + \nabla \cdot \mathbf{E}\nabla\frac{\delta F}{\delta \mathbf{w}}. \tag{153}$$

where $\mathbf{N} = \mathbf{AMA}$ and $\mathbf{E} = \mathbf{ADA}$. If we assume that both $v_1, v_2 \in [0,1]$ and $w_1, w_2 \in [0,1]$ this means that the transformation is limited to

$$\mathbf{A} = \begin{bmatrix} a & 1-a \\ 1-a & a \end{bmatrix} \tag{154}$$

If furthermore we limit our transformation so that both $v_2(= c)$ and w_2 are conservative we are left with $\mathbf{A} = \mathbf{I}$ and $w_i = v_i$.

We conclude that cross terms do not naturally arise from a linear transformation of variables and hence that the introduction of cross terms is indeed a change to the model.

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