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# A novel route to the coupling of molecular dynamics and phase-field simulations of crystal growth

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## Abstract

Molecular dynamic simulations, *ab initio* (DFT) calculations and experimental evidence suggests that there is a liquid-solid transition region which may be characterised by an order parameter. In this interface region the order parameter is not observed to be symmetrical, rather it tends to be steep on the solid side and exponentially decreasing on the liquid side. The order parameter in phase field computations is, to date, always assumed to give a symmetrical interface region. Hence, we ask how to extend the phase field model to give a profile that fits this data, and how such a model affects the simulation.

Keywords: crystal formation; diffuse interface; alloy solidification;

## 1 Introduction

The integration of modelling techniques that operate on disparate length and timescales is one of the greatest challenges facing the computational simulation of materials. At the atomistic scale techniques such as density functional theory (DFT) and molecular dynamics (MD) track every atomic degree of freedom but are severely limited with regard to the size of domain that can be considered. The largest such MD simulations reported [1, 2], facilitated by massively parallel supercomputers, contain  $O(10^{12})$  atoms (in MD, very significantly less in DFT) wherein, for an example material such as metallic Ni at standard temperature and pressure, we have a simulation volume of  $\approx 10^{-17}\text{m}^3$ . Conversely, continuum models cover length scales from the mesoscale ( $10^{-6}$  to  $10^{-4}\text{m}$ ), with techniques such as phase-field modelling [3] and level sets [4]) to that of large engineering structures and beyond.

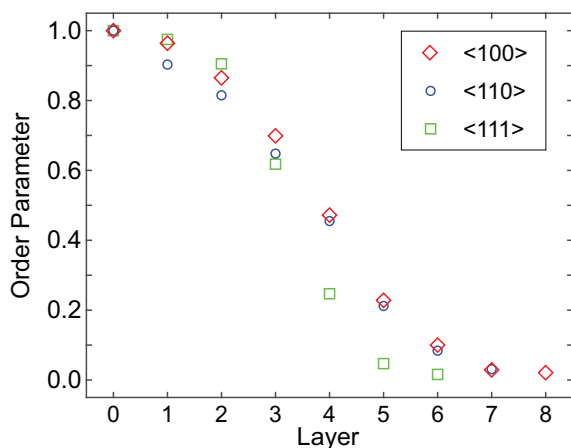
Linking these length scales is critically important to the quantitative understanding of material behaviour. However, to date most such linking is of the ‘weak’ type, that is, parameters or constitutive equations derived from models at small length or timescales are incorporated into models operating at larger scales. For instance, a cascade of such weak coupling from the atomistic to the component scale, is described by [5], in which results obtained from DFT models of dislocation core structures are used to describe solute strengthening in FE models of the tensile deformation of aluminium alloys. Strong coupling, in which models operating at disparate length scales are directly linked, is much rarer, particularly with regard to linking from the atomistic to the continuum scale (but see [16]). With regard to fluid dynamics Neumann *et al.* [6] stated “only one framework-like piece of software has been developed so far for ... coupling molecular-continuum code”, while in the solid-state [7] present a rare example of an embedded atom model for a Co-Ni-Al particulate being incorporated into an FE model of an aluminium matrix.

Solidification is a phenomena that intrinsically bridges multiple length scales with crystallisation morphologies being determined both by macroscale diffusive-convective fluxes of heat and solute and atomistic scale capillary and kinetic effects [8]. Despite this there are remarkably few examples of models coupling across the atomistic-continuum divide. There are a few examples of weak coupling (e.g. [9]) in which capillary and kinetic parameters derived from MD simulations are fed into mesoscale phase-field simulations but, as far as we are aware, this is the extent of coupling across the atomistic-continuum divide in the field of crystallisation. Note that we explicitly exclude from this definition models of the phase-field crystal (PFC)



type as, while these model discrete atom positions by means of a continuous density function, the length scales modelled are comparable to large MD simulations.

Within solidification modelling, phase-field simulation is one of the most popular and successful continuum techniques for modelling microstructure formation. In fact there exists a very natural route to linking phase-field and atomistic simulations such as MD, via the structure of the diffuse interface. The interface between the solid and the liquid is modelled via an order parameter,  $\phi$ , which varies continuously between 1 in the solid and 0 in the liquid over some finite interface width. When we look at MD simulations of a solid-liquid interface we see just such a progressive transition, with crystalline order being lost over an interface width of several atom diameters. There are various ways in which this loss of order can be parameterised, for instance using an in-plane order parameter or via the locus of the density maxima across the interface. The in-plane order parameter, calculated via MD for the growth of Al from its parent melt along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$  directions, is shown in Figure 1. It is clear from the figure that the effective interface width (i.e. the number of atom planes over which long-range crystalline ordering is lost) varies with growth direction, with the width of the  $\langle 111 \rangle$  interface being significantly smaller than for growth in either the  $\langle 110 \rangle$  or  $\langle 100 \rangle$  directions.



**Figure 1.** In plane order parameter for the growth of Al in the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$  direction at 880K (53K undercooling) as calculated by molecular dynamics.

The atomic structure of the proximal liquid to a solid crystalline interface has been the subject of considerable recent interest [14], with liquid atoms becoming layered due to the crystalline order within the solid. However, the asymmetry in the interface, i.e. that order is lost rapidly in the first 1-2 liquid layers but that vestiges of ordering persist several layers out, has only recently become apparent. [see e.g. Fig. 2 in Ref. [15]. This asymmetry appears to be due to a large number of defects being introduced into the first layer adjacent to the solid, with a more gradual increase in defect density thereafter, although phenomenon has been far from fully explored.

In most cases the phase-field diffuse interface is taken as a tanh profile, the form of which is  $\phi = \frac{1}{2} - \frac{1}{2} \tanh((x - x_0)/\delta)$  where  $x_0$  is the interface position and  $\delta$  the interface width. However, this is generally no more than a computational expedient, with no attempt made to match either the shape or length scale to what might be considered realistic values from MD simulation. Over the last several years we have shown how the application of advanced numerical techniques such as adaptive mesh refinement, implicit time-stepping, non-linear multigrid solvers and parallelisation allows realistic interface widths to be used in phase-field simulation [3, 10, 11, 12]. We now turn our attention to the shape of the interface. It can be seen from Figure 1 that, irrespective of the growth direction, the in-plane order parameter decreases more steeply on the solid side of the solid-liquid interface than on the liquid side. In fact, the MD simulation interface can be parameterised by a tanh curve only if we take  $\delta$  to be different on the solid and liquid sides of the interface. As an example, the profile for growth along the  $\langle 110 \rangle$  direction can be parameterised by a tanh curve if  $\delta = 2.65(0.5 \leq f < 1)$  and  $\delta = 3.54(0 < \phi \leq 0.5)$ . This is in stark contrast to phase-field, where a symmetry around  $\phi = 0.5$  is assumed. Our contention here is that additional physics can be captured by matching the phase-field interface to the shape and length-scale predicted by atomistic simulations of the solid-liquid interface. We present below a phase-field formalism that allows an arbitrary monotonic order parameter to be matched in the interface region.

## 2 Phase field fitting to MD data

The question we wish to address is: given a set a data from *ab-initio* or molecular dynamic simulation how can we model this within phase field? We begin by assuming we have a given phase field profile,  $\phi(x)$ , which is determined in advance by measurements from MD data. Within a phase field model, this profile is determined by a double well potential,  $f(\phi)$ , as part of the equilibrium equations:

$$\frac{\delta F}{\delta \phi} = 0 \quad (1)$$

where

$$F = \int \delta^2 \nabla \phi \cdot \nabla \phi + f. \quad (2)$$

Computing the variational derivative gives

$$\frac{\delta F}{\delta \phi} = -\delta^2 \nabla^2 \phi + \frac{\partial f}{\partial \phi} = 0 \quad (3)$$

which, in 1D reduces to

$$\delta^2 \phi''(x) = \frac{\partial f}{\partial \phi}. \quad (4)$$

This can be written

$$\delta^2 \frac{\partial}{\partial x} \frac{\partial \phi}{\partial x} = \frac{\partial f}{\partial \phi} \quad (5)$$

Now  $\frac{\partial \phi}{\partial x} = 1/\frac{\partial x}{\partial \phi}$  and so by the chain rule

$$\begin{aligned} \frac{1}{\delta^2} \frac{\partial f}{\partial \phi} &= \frac{\partial}{\partial x} \frac{\partial \phi}{\partial x} = \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi} \left( \frac{\partial \phi}{\partial x} \right) = \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi} \left( \frac{\partial x}{\partial \phi} \right)^{-1} \\ &= -\frac{\partial \phi}{\partial x} \left( \frac{\partial x}{\partial \phi} \right)^{-2} \frac{\partial^2 x}{\partial \phi^2} \\ &= -\left( \frac{\partial x}{\partial \phi} \right)^{-3} \frac{\partial^2 x}{\partial \phi^2} \\ &= \frac{\partial}{\partial \phi} \left[ \frac{1}{2} \left( \frac{\partial x}{\partial \phi} \right)^{-2} \right] \end{aligned} \quad (6)$$

and thus

$$f = \frac{\delta^2}{2} \left( \frac{\partial x}{\partial \phi} \right)^{-2}. \quad (7)$$

For example, the standard, symmetrical, 1D phase field solution

$$\phi = 1/2 \left[ 1 + \tanh \left( \frac{x}{\sqrt{2}\delta} \right) \right] \equiv \frac{1}{1 + \exp(-\sqrt{2}x/\delta)} \quad (8)$$

which has inverse

$$x = \frac{\delta}{\sqrt{2}} [\ln(\phi) - \ln(1 - \phi)] \quad (9)$$

determines the double well potential:

$$f = \frac{\delta^2}{2} \left( \frac{\partial x}{\partial \phi} \right)^{-2} = \phi^2(1 - \phi)^2. \quad (10)$$

Notice in the above, we required the inverse function  $x = x(\phi)$ , which is easily obtainable by fitting to data of the form

$$[[x_0, \phi_0], [x_1, \phi_1], \dots, [x_n, \phi_n]]. \quad (11)$$

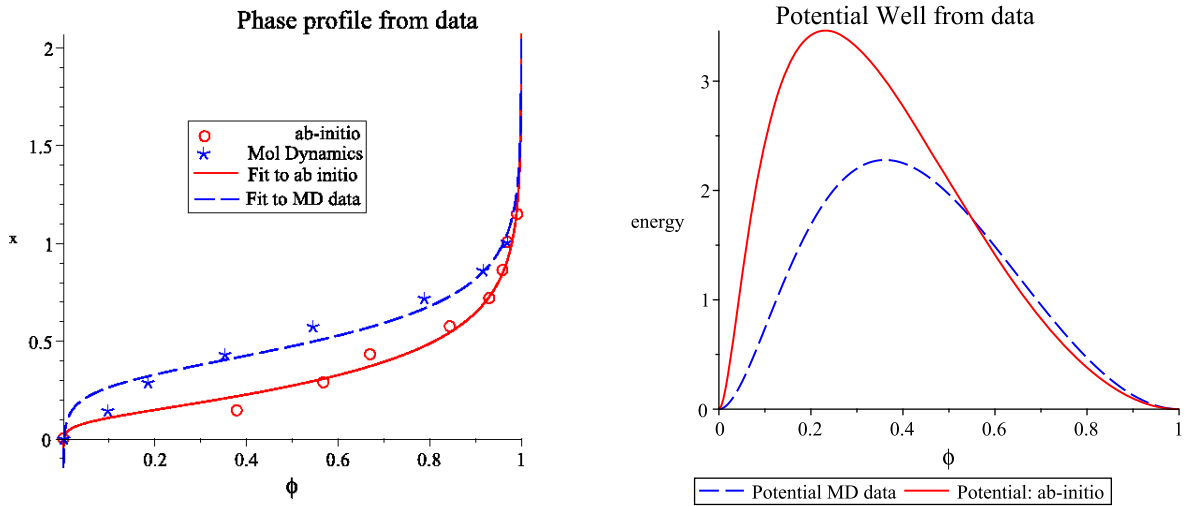
By choosing a function to fit the data carefully we will be able to retain some desirable properties of the potential. We impose the property of  $x(\phi)$  that

$$1/x'(0) = 1/x'(1) = 0 \quad (12)$$

Keeping in mind the function for the symmetric profile, Eq. 9, we choose the simplest ansatz for an arbitrary position

$$x(\phi) = a \ln(\phi) + b \ln(1 - \phi) + c \quad (13)$$

where the constants  $a, b, c$  are determined from the data by least squares. Clearly if  $a = -b$  we return the symmetrical tanh phase profile with some interface width (determined by  $a$ ) and position along the x-axis (determined by  $c$ ). Our fit to one of the sets of data from Figure 1 is shown together with the corresponding potential wells in Figure 2. Also shown, to demonstrate that profiles with a more extreme skew can be accommodated, is a fit to the interface for Al nucleated on a static substrate calculated via ab-initio simulation. Note, that the data here is more usefully presented as  $x$  as a function of phase,  $\phi$ .



**Figure 2.** Fitted data (crosses and circles) using Eq. 13, determines the potential wells on the right in corresponding colour and line style. In line with phase field convention, we choose  $\phi = 0$  to be solid (in contrast to the convention in Figure 1), and we fit the  $\langle 110 \rangle$  data from that figure (blue stars) along with some heavily skewed DFT data (red circles). The more non-symmetrical the data, the more skewed the double well potential,  $f(\phi)$ . Notice that the the less symmetry in the ab initio data (red circle) gives the more skewed potential well (red solid line).

### 3 Interpolation function

We now have a method by which we can reproduce a fitted curve that approximates given experimental or *ab initio* computations, by determining the appropriate double well potential for an equilibrium solution. However, for a non-equilibrium solution it is not sufficient to only modify the double well potential. We find that it is necessary to modify the forcing term also. The key function for this is the interpolation function,  $g(\phi)$ , which arises in the energy,

$$F = \int \delta^2 \nabla \phi \cdot \nabla \phi + f(\phi) + g(\phi) f_L(c, T) + (1 - g(\phi)) f_S(c, T), \quad (14)$$

where  $f_L, f_S$  are the free energies of the pure liquid and pure solid respectively obtained, for example, from a thermodynamic data base. Typically, the interpolation function,  $g(\phi)$ , used in phase field is constructed from the double well potential (e.g. Wheeler)

$$g'(\phi) = C \int f(\phi) d\phi \quad (15)$$

where  $C$  is some constant and  $g(0) = 0, g(1) = 1$ . This would make  $g$  a 5<sup>th</sup> order polynomial if the double well potential,  $f(\phi)$ , is the standard 4<sup>th</sup> order form. We do not adopt this and instead relate  $g$  to a moving tanh profile,

$$\phi = \frac{1}{2} \left[ 1 + \tanh \left( \frac{2(x - Vt)}{\delta} \right) \right] \quad (16)$$

where  $V$  is the speed in which this profile is moving to the right. We require

$$\dot{\phi} = -Cg'(\phi) \quad (17)$$

for some positive constant  $C$ . We find

$$\dot{\phi} = -4V\phi(1 - \phi)/\delta \quad (18)$$

which gives the (normalised) cubic polynomial

$$g = \phi^2(3 - 2\phi), \quad (19)$$

and so

$$\dot{\phi} = -4V\phi(1 - \phi)/\delta = -\frac{2V}{3\delta}g'(\phi). \quad (20)$$

We may note that, in this case, it appears to suggest the rule

$$g'(\phi) \propto \sqrt{f(\phi)}. \quad (21)$$

If this is generally true we can apply this rule to obtain  $g(\phi)$  from any  $f(\phi)$ . So, assume both

$$\frac{d^2\phi}{dx^2} = \alpha(\phi), \quad \frac{d\phi}{dx} = \beta(\phi) \quad (22)$$

where clearly  $\alpha(\phi) = f(\phi)/\delta^2$  and  $\beta(\phi) \propto g'(\phi)$ . It follows that

$$\alpha(\phi) = \frac{d^2\phi}{dx^2} = \frac{d\beta}{dx} = \frac{d\beta}{d\phi} \frac{d\phi}{dx} = \frac{d\beta}{d\phi} \beta = \frac{1}{2} \frac{d(\beta^2)}{d\phi} \quad (23)$$

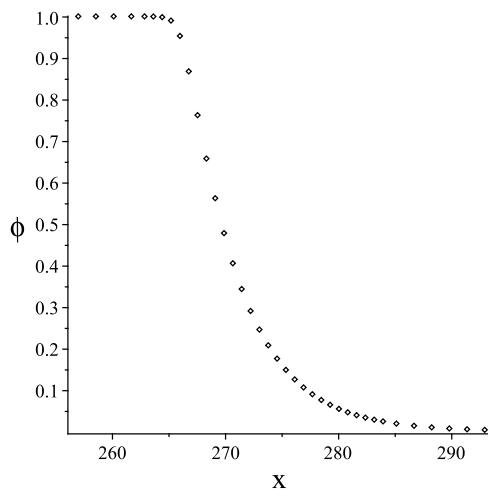
Hence, in general,  $f \propto [g'(\phi)]^2$ . and so

$$g = C \int \sqrt{f(\phi)} d\phi \quad (24)$$

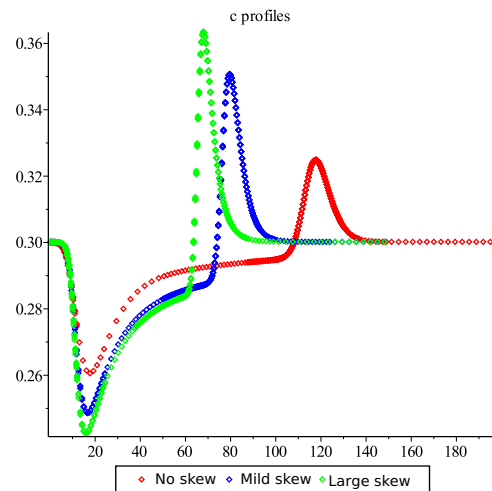
where  $C$  is chosen so that  $g(0) = 0, g(1) = 1$ .

## 4 The effect of phase profile on solute partitioning

Figure 3a illustrates a phase field example of a skewed profile. The use of skewed profiles necessarily changes the dynamics of the model, for example, using a series of increasingly skewed profiles affects the solute partitioning at the interface- see Figure 3b.



**Figure 3a** A phase field simulation using a large skew double well potential



**Figure 3b** A series of increasingly skewed phase profiles from red (symmetrical) to very skewed blue to green.

## 5 Summary

We have described a procedure whereby we can use external data to dictate the profile shape in a phase field model. This involves using a least squares fit to a limited function with only three free coefficients. Once this function is known we describe how to obtain the interpolation function so that the profile shape is maintained even under non equilibrium conditions. There is some evidence that profile shape affects the dynamics although it is hard to isolate these from effects due to reduction in interface width.

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