

A Method of Calculating the Thickness of a Solid-Liquid Interface

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Abstract

Microstructural evolution is a phenomenon of paramount importance in various areas of industry; its understanding is critical for designing materials with superior properties. The nonlinear and metastable nature of this mesoscale phenomenon has given rise to various models that attempt to describe it. One type of model that is often used is a phase-field model. Here we present a method to determine a constant related to the solid-liquid interface thickness found in the model via atomistic simulation.

1 Introduction

In order to understand what a solid liquid interface is and why its thickness is significant, consider the following characterization of a pure material at its equilibrium melting temperature. If you were to look at the liquid phase at a very small scale you would ‘see’ atoms that are randomly distributed. If you were to count the number of atoms that are inside some box, the amount you count would only vary with the size of the box you choose, not the location of it. However, if you were to do the same thing in the solid phase, the number of atoms in a box would vary with the location of the box as well as the size of the box. This is because in a solid, atoms are no longer distributed randomly; they are positioned on a crystal lattice. This lattice consists of planes of atoms that are parallel to each other. Therefore, a slight change in the position or size of the box could lead to a large change in the number of atoms in the box. When a metal melts or solidifies (freezes), it makes a transition from solid to liquid or vice versa. When examining a liquid-solid phase transition in metals, if one looks at the boundary that separates the two phases on a very small scale, there is a region of atoms between the two phases that reconciles the random distribution of atoms in the liquid region and the crystalline structure of atoms in the solid region. This region is neither wholly randomly distributed nor wholly aligned along lattice planes; this region is known as a solid-liquid interface.

The thickness of this region is significant, especially in modelling phase transitions at small scales; many different models use this thickness as a parameter

to calibrate the model [1]. Therefore, the accuracy of models that use this parameter is affected by the accuracy of this parameter. In the case of modelling copper, people often choose 5\AA as an estimate for the parameter [10]; however, the exact thickness of the solid-liquid interface is not known. One reason this thickness is not known is that it is dependent on the orientation of the crystal lattice. In this work, we only consider the $\langle 110 \rangle$ orientation which allows us to assume that lattice planes are perpendicular to one coordinate axis and parallel to the other two axes [11].

A way to more rigorously obtain an estimate of the interface thickness would be to take a phase-field model which uses the interface thickness as a parameter and fit this model to experimental data. Since experiments at this small scale are expensive and difficult to construct, here we will use a *numerical experiment* instead. The term *numerical experiment* refers to a computer simulation which simulates an actual experiment [3]. The *numerical experiment* we present in this work simulates individual atoms and calculates their positions as these atoms approach thermodynamic equilibrium. Below, we first describe the phase-field model. We then describe the *numerical experiment*. Then the method of how to obtain an estimate of the interface thickness from these models is explained.

1.1 Phase-Field Model and the Order Parameter

The model that we will fit to a *numerical experiment* is a phase-field model [1, 2]. Phase-field models use an order parameter $\phi(x)$ to describe the phase (e.g. solid or liquid) at a given position. We define $\phi = 0$ when the material is solid and $\phi = 1$ when the material is liquid. The order parameter is assumed to be a twice continuously differentiable function of position x over the entire domain. For simplicity, we only consider a 1-dimensional case where the x -axis is perpendicular to the lattice planes. When $\phi \in (0, 1)$, we provide an atomistic physical interpretation, i.e. the order parameter is a normalized envelope for the probability of finding an atom at a given position, Figure 1.

Here, we only consider pure materials (e.g. copper) which are isothermal at their melting point. The free energy of this system F is defined by the functional

$$F = \int \left[f(\phi) + \frac{\epsilon}{2} \left(\frac{\partial \phi}{\partial x} \right)^2 \right] dx, \quad (1)$$

where ϵ is the gradient energy coefficient, and $f(\phi)$ is a ‘double well’ free energy density function which describes the free energy penalty incurred where the material is in an intermediate phase

$$f(\phi) = W\phi^2(1 - \phi)^2, \quad (2)$$

where W is a parameter that scales f for specific materials [1]. By creating a free energy penalty where $\phi \neq 1$ or $\phi \neq 0$, this term makes the intermediate phases described by the order parameter energetically unstable. The derivative term in (1), $\epsilon/2(\partial\phi/\partial x)^2$, makes a sharp interface, i.e. an interface where there are no intermediate phases, energetically unstable by imposing a large energy

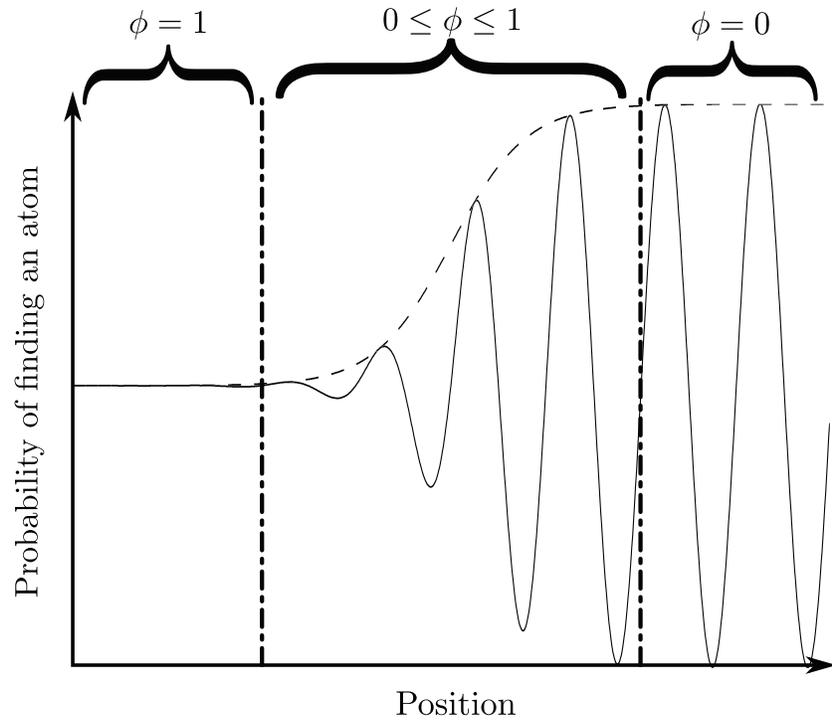


Figure 1: An atomistic interpretation of the order parameter, ϕ . The solid line represents the probability of finding an atom at that position; the dashed line is the envelope of this curve which will allow us to quantify the phase of the material at a given position. In the region marked as $\phi = 1$, the probability of finding an atom at a given location is uniform throughout the region, indicative of liquid. In the region labeled as $\phi = 0$, the probability of finding an atom varies extremely throughout the region corresponding to the crystal lattice of the material. (Adapted from Mikheev & Chernov, 1991)

penalty when $|\partial\phi/\partial x|$ becomes large. Since we assumed that the material is isothermal at the melting point, we are only concerned with the coarsening that takes place as the different phases in the material come to equilibrium. In order to find equilibrium, we must find a $\phi(x)$ which minimizes the free energy F . To find such a $\phi(x)$ that minimizes F , we use the calculus of variations [6]. This yields the Euler-Lagrange equation

$$0 = \epsilon^2 \frac{\partial^2 \phi}{\partial x^2} - \frac{df}{d\phi}. \quad (3)$$

Subject to boundary conditions $\phi \rightarrow 0$ as $x \rightarrow -\infty$ and $\phi \rightarrow 1$ as $x \rightarrow \infty$, this differential equation has the analytical solution

$$\phi(x) = \frac{1}{2} \left[1 + \tanh \left(\frac{x}{2\delta} \right) \right], \quad (4)$$

where δ^1 is the solid-liquid interface thickness [1]. It is this solution that will later be fit to the data from a *numerical experiment* in order to calculate the interface thickness.

1.2 Numerical Experiments

In the *numerical experiments*, we calculate the positions of atoms in a block of partially melted copper at thermodynamic equilibrium. This is achieved by generating an initial block of copper atoms and applying the Metropolis Algorithm to the block. One iteration of the algorithm is given below [4].

1. Compute the total energy E_1
2. Randomly choose an atom a
3. Move a in a random direction by a random distance
4. Compute the total energy after the move E_2
5. If $E_2 - E_1 < 0$, accept the move
6. Otherwise:
 - Compute $p = \exp \left[\frac{E_2 - E_1}{-k_B T} \right]$ where k is Boltzmann's constant and T is the uniform temperature of the *numerical experiment*
 - Randomly generate $r \in [0, 1)$
 - If $r \leq p$, accept the move.

¹The definition we have used for δ is inherited from (4). There are other ways to define δ which are multiples of the definition we have used [2].

The energy computation referenced in the algorithm is done using an embedded-atom method which accurately recreates many of the material properties of copper [5]. We describe a few details of this method below. First, we note that this method predicts a different melting point for copper (1327 K) than the experimentally determined value (1358 K). This must be taken into account in the temperature used in the algorithm since the *numerical experiment* is conducted at its associated melting point (1327 K).

The simulation block in Figure 2 was generated using atomistic simulations². First a block was generated at 0K with lattice orientation $\langle 110 \rangle$. By choosing the $\langle 110 \rangle$ lattice orientation, the atomic planes will be perpendicular to the x -axis in Figure 2. The block was created so that there would be a vacuum at each end of the block. Then the block was heated beyond the melting point and expanded (to account for temperature dependence of volume) so that liquid regions would appear at the ends of the block while keeping a solid region in the middle. From here, the block was cooled back to the melting point and approached equilibrium via 3000 iterations of the above algorithm. The configuration of the block was saved at each iteration from 3001 to 3250. In order to check that the block was sufficiently close to equilibrium, we checked the following condition for these 250 snapshots.

$$|E_i - E_j| < 1\% E_{\text{avg}}, \quad (5)$$

where E_i is the total energy of snapshot i , E_j is the total energy of snapshot j , and E_{avg} is the mean total energy of these 250 snapshots. These 250 snapshots of the block configuration constitute the data to which we apply our method in the next section.

2 Method

The method of fitting the solution of the phase-field model, (4), to the *numerical experiment* in order to estimate the solid-liquid interface thickness consists of three parts: finding a number density profile from the *numerical experiments*, finding an envelope of this number density profile, and fitting the envelope to the solution of the phase-field model, (4).

2.1 Finding the Number Density Profile

In order to interpolate the order parameter from the atomistic data, we must first find a value for number density η , i.e. the probability of finding an atom at a given position along the spatial dimension. To do this, we calculate

$$\eta(x) = \sum_{i \in \text{atoms}} e^{-\sigma(x-x_i)^2} \quad (6)$$

where x_i is the projection of the position of the i th atom onto the x -axis; the units of x and x_i are Å. σ appears in (6) in order to scale the units of $(x-x_i)^2$,

²Specifically, we used the program SOLD, which was developed by Y. Mishin (private communication, 2009).

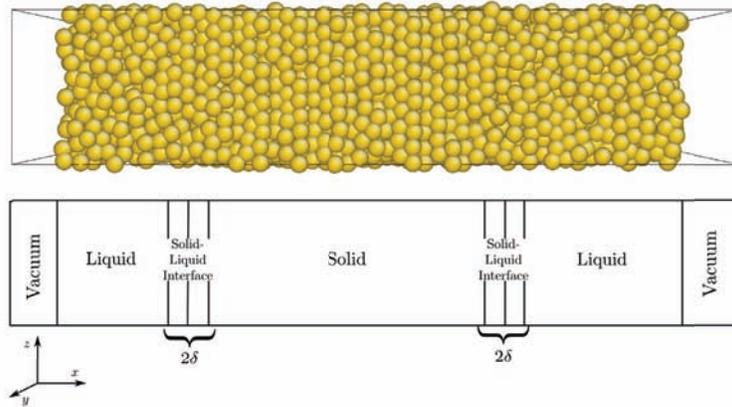


Figure 2: Simulation block. δ is the interface thickness. Figure generated with Atomeye [7]

so it has units \AA^{-2} ; the specific value chosen for σ will be explained later. We have used a Gaussian function in (6) in order to smooth out the data. Since atoms do not exist as point particles, this Gaussian function is used to smooth the atoms by weighting their presence along the domain [9]. Since we assumed that atomic planes are perpendicular to the x -axis and parallel to the yz -plane when plotted, $\eta(x)$ is a damped wave. A typical case is pictured in Figure 3. High amplitude in the middle region of Figure 3 is indicative of a solid region since large oscillations in number density reflect the existence of a crystal lattice, while low amplitude in the far left and far right regions of Figure 3 is indicative of a liquid region since the atoms are distributed uniformly across the region [8]. Thus, by identifying regions of relatively high or relatively low amplitudes, we can determine where a material is liquid or solid. If we had not made the assumption about the positioning of the atomic planes, the planes would overlap and the higher amplitude would not be present in the solid region. Furthermore, the formation of these regions of higher or lower amplitude is dependent on the value we choose for σ . σ should be approximately the distance between lattice planes, so for the $\langle 110 \rangle$ orientation, we chose $\sigma = 2$. If σ is too small, the number density profile will have high amplitude throughout the entire block; if σ is too large, the number density profile will have low amplitude throughout the block. The sensitivity of this method to σ is an interesting topic for future work but is not discussed here.

2.2 Finding the Envelope of the Number Density Profile

The envelope of the number density $\eta_{\text{env}}(x_i)$ is a function that maps the positions of the stationary points of $\eta(x)$, i.e. $S = \{x | \eta'(x) = 0\}$ (peaks and valleys

of the wave) to the interval $[0, 1]$. The definition of $\eta(x)$, (6) ensures that $\eta(x)$ is at least twice differentiable. Figure 3 shows an example number density profile with the stationary points marked by 'x'. We define this function via the following. Let $\eta_{\max}(x_i)$ be the function mapping the positions of local maxima of $\eta(x)$, i.e. $P^+ = \{x_i \in S | \eta''(x) < 0\}$ (the peaks of $\eta(x)$) to their corresponding values of η . $\eta_{\min}(x_k)$ is defined similarly, but for the local maxima of $-\eta(x)$, i.e. $\eta_{\min}(x_i)$ maps $x_i \in P^- = \{x_i \in S | -\eta''(x) < 0\}$ to $-\eta(x_i)$. We now scale $\eta_{\min}(x_i)$ and $\eta_{\max}(x_i)$ to be in $[0, 1]$

$$\eta_{\text{env}}(x_i) = \begin{cases} \frac{\max_{x_i}(\eta_{\min}(x_i) - \min_{x_i} \eta_{\min}(x_i)) - \eta_{\min}(x_i) + \min_{x_i} \eta_{\min}(x_i)}{\max_{x_i}(\eta_{\min}(x_i) - \min_{x_i} \eta_{\min}(x_i))} & \text{if } x_i \in P^- \\ \frac{\max_{x_i}(\eta_{\max}(x_i) - \min_{x_i} \eta_{\max}(x_i)) - \eta_{\max}(x_i) + \min_{x_i} \eta_{\max}(x_i)}{\max_{x_i}(\eta_{\max}(x_i) - \min_{x_i} \eta_{\max}(x_i))} & \text{if } x_i \in P^+ \end{cases} \quad (7)$$

By constructing $\eta_{\text{env}}(x_i)$ in this way, the local maxima of $\eta(x)$ are flipped and scaled while the local minima of $\eta(x)$ are flipped twice and scaled. By including both the local minima and the local maxima of $\eta(x)$ in our envelope, we obtain a higher resolution envelope than we would if we only used the local maxima of $\eta(x)$ alone.

2.3 Fitting the Envelope

$\eta_{\text{env}}(x)$ is now fitted to an analytical solution of the phase-field model (4) via a five parameter non-linear least squares fit which minimizes

$$\min \left\| \eta_{\text{env}}(x) - p_1 \left(\frac{1}{2} \tanh \left(\frac{x - p_2}{2\delta} \right) - \frac{1}{2} \tanh \left(\frac{x - p_3}{2\delta} \right) + 1 \right) + p_4 \right\|_2, \quad (8)$$

where the five parameters are:

1. δ the interface thickness
2. p_1 a vertical scaling parameter
3. p_2 a location of the right interface
4. p_3 a location of the left interface
5. p_4 a vertical shifting parameter

An example of this fitting procedure for a specific snapshot can be seen in Figure 4. However, in order to ensure the precision of this method, we must consider more than just one snapshot.

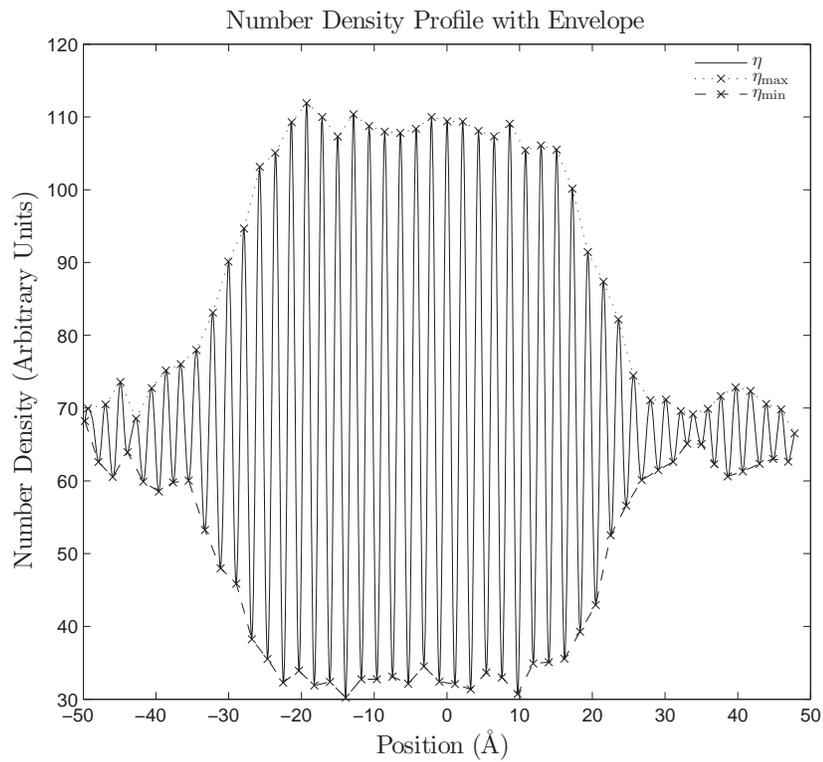


Figure 3: The solid line represents the number density profile, $\eta(x)$. The local maxima and minima marked of the density profile are marked as 'x'. The vertical scale in this figure is not significant. Take note that the $\eta_{\min}(x_i)$ plotted is actually $-\eta_{\min}(x_i)$ as defined earlier.

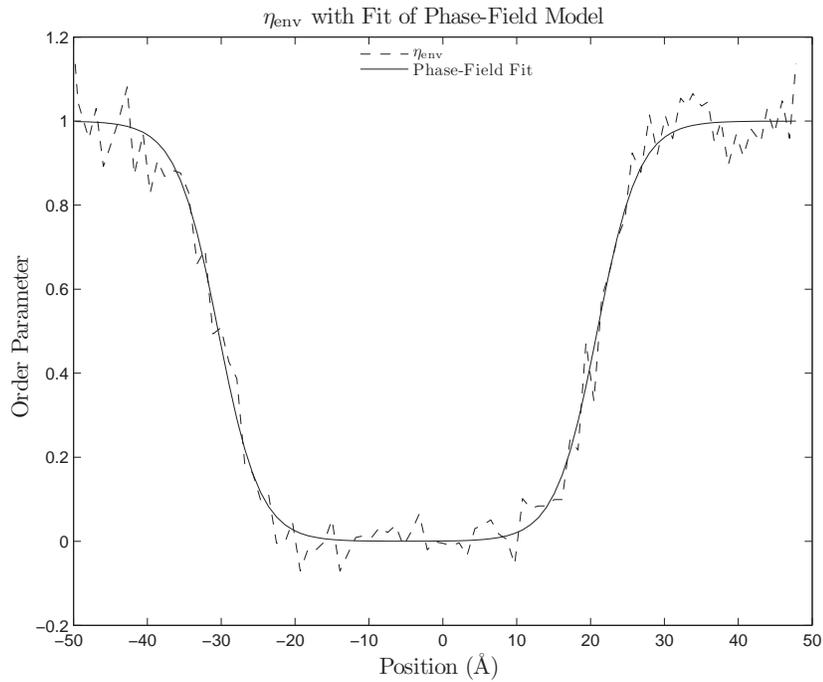


Figure 4: A fit of $\eta_{\text{env}}(x)$ to the analytical solution of the phase-field model (4) with $\delta = 2.86\text{\AA}$ taken from the result of (8) for a specific snapshot; (9) is the result averaged over all snapshots. The units in the vertical axis of this plot are chosen so that they agree with the solution of the phase-field model. For the sake of readability, we have scaled η_{env} so that what is plotted is actually $(\eta_{\text{env}} - p_4)/p_1$ where p_1 and p_4 are taken from (8).

3 Results and Conclusion

For each snapshot taken after the simulation block has been equilibrated, we calculate the value for δ given in (8) and average these values. When using this method to calculate the solid-liquid interface thickness for copper, we find

$$\delta = 2.93 \pm .27\text{\AA}, \quad (9)$$

where the uncertainty of δ is given by the standard deviation of the average. This number slightly disagrees with previous estimates of interface thickness for copper of 5\AA . One potential source of disagreement is that the interface thickness is dependent on the orientation of the crystal lattice. The atomistic simulations were set up to handle the $\langle 110 \rangle$ orientation. By using this orientation, the lattice planes are perpendicular to the x -axis and parallel to the yz -plane. This assumption on the positioning of the lattice planes is an assumption that the method outlined in section 2 relies upon. In order to calculate the interface thickness for different crystal orientations, the method will need to be modified in a nontrivial way. In spite of this limitation, the method does produce a reasonable estimate for the interface thickness of copper that may increase the accuracy of models that are being used today.

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