Interfacial free energy and stiffness of aluminum during rapid solidification

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Abstract

Using molecular dynamics simulations and the capillary fluctuation method, we have calculated the anisotropic crystal-melt interfacial free energy and stiffness of aluminum in a rapid solidification system where a temperature gradient is applied to enforce thermal non-equilibrium. To calculate these material properties, the standard capillary fluctuation method typically used for systems in equilibrium has been modified to incorporate a second-order Taylor expansion of the interfacial free energy term. The result is a robust method for calculating interfacial energy, stiffness and anisotropy as a function of temperature gradient using the fluctuations in the defined interface height. This work includes the calculation of interface characteristics for temperature gradients ranging from 11~34 K/nm. The captured results are compared to a thermal equilibrium case using the same model and simulation technique with a zero gradient definition. We define the temperature gradient as the change in temperature over height perpendicular to the crystal-melt interface. The gradients are applied in MD simulations using defined thermostat regions on a stable solid-liquid interface initially in thermal equilibrium. The results of this work show that the interfacial stiffness and free energy for aluminum are dependent on the magnitude of the temperature gradient, however the anisotropic parameters remain independent of the non-equilibrium conditions applied in this analysis. The relationships of the interfacial free energy/stiffness are determined to be linearly related to the thermal gradient, and can be interpolated to find material characteristics at additional temperature gradients.

Keywords: rapid solidification; molecular dynamics; solid-liquid interface, interfacial stiffness; interface free energy

1 Introduction

The study of rapid solidification through computational analyses has seen an increase in demand due to the recent advances in the additive manufacturing industry. These processes apply extreme temperature gradients to propagate the interface between the solid and liquid phases of the material to form a new microstructure. The extreme environmental impacts on the material often result in the development of intrinsic defects that contribute to the degradation of the material strength and limit the applications of these structural components [1-4]. For standard solidification phenomena, multi-scale simulations provide us with a means to study the formation of these microstructures at an atomic scale, as well as the progression and impact of these defects through phase-field and finite element method simulations [5-9]. When these theories are applied to rapid solidification processes, the assumption of thermal equilibrium may not result in the most accurate representation of the physical state [10-13]. This paper focuses on the atomic scale of the rapid solidification of aluminum through molecular dynamics with the application of the capillary fluctuation method and an applied thermal gradient that drives the system out of equilibrium to capture the changes in the interface characteristics.

The strength of metallic structures formed through solidification processes is largely affected by the growth patterns of microstructures known as dendrites. These crystalline structures are the result of a moving solid-liquid interface and are constrained by the fluctuating

heating and cooling temperatures[7, 11, 14-17]. For standard solidification processes, such as welding, the geometric growth patterns of these dendrites have been shown to be dependent primarily on the individual tip velocity and interfacial stiffness for the material[5, 18]. These patterns are typically studied through phase-field simulations using an equilibrium-based Gibbs-Thomson condition, oftensupplemented with results from molecular dynamic (MD) simulations. However, for rapid solidification processes, where the heating and cooling rates can be on the order of 10^3 - 10^8 K/s[19], the structures are formed through extreme thermodynamic environments forcing the crystal melt interface into a non-equilibrium state quantified by temperature and composition gradients across the interface. Concerning temperature, to understand how its profile might affect the phase-field simulations, we must first derive theequilibrium assumptions in the Gibbs-Thomson condition.

The Gibbs-Thomson condition in two-dimensions[6, 15, 17, 20, 21] relates the temperature at the interface, T_i , to the deviation from the melting temperature, T_m , caused by the curvature and velocity of the interface, $T_i = T_m - \frac{T_m}{L} \sum_{i=1,2} [\gamma(\hat{n}) + \gamma(\hat{n})_{\theta\theta}] \frac{1}{R_i} - \frac{V_n}{\mu(\hat{n})}$, where L is the latent heat, $\gamma(\hat{n})$ is the interfacial free energy, θ_i are the local angles between the normal direction n , and the two principle directions and R_i is the principle radii of curvature. The final two terms, V and μ , are the normal velocity of the interface and kinetic coefficient respectively. The Gibbs-Thomson condition defines the interfacial stiffness, $\gamma(\hat{n}) + \gamma(\hat{n})_{\theta\theta}$, in equilibrium where it is independent of thermal gradients. However, recent studies of solid-solid phase interactions using the capillary fluctuation method[22, 23] have shown that the interfacial stiffness is indeed dependent on the thermal conditions. In rapid solidification processes, where temperature gradient and interface velocity define the microstructure, it is necessary to define an interfacial stiffness in terms of both normal orientation and temperature gradient.

In this paper, we use MD simulations to apply non-equilibrium thermal conditions through temperature gradient profiles perpendicular to the interface and calculate the interfacial free energies, stiffness and anisotropic characteristics for a pure aluminum structure. These interfaceproperties, calculated through the capillary fluctuation method CFM[24], are compared to a thermal equilibrium case when the gradient is zero and the structure temperature is set to the melting temperature. From the data, we candevlop material specifictemperature gradient-dependentrelationships for interfacial stiffness and free energy. These properties can be used in subsequent multi-scale computational studies where interfacial stiffness and energy are key parameters.

2 Theory

There have been various methods developed to study interfacial properties in molecular dynamic (MD) simulations. For solid-liquid solidification systems in equilibrium, the interfacial stiffnessis often calculated using the capillary fluctuation method (CFM)[25-27] on a thin quasi-2D system. This method relatethe interfacial stiffness to the mean square amplitude, $h(x) = \sum_k A(k)e^{ikx}$, through equipartition and Fourier mode analysis such that:

$$\langle |A(k)|^2 \rangle = \frac{k_b T_\sigma}{bW(S(\theta))k^2} \quad (1)$$

where k_b is the Boltzmann constant, T_σ is the temperature of the system, W is the width, b is the thickness, k is the wavenumber, γ represents the interface free energy and θ if the angle between

the interface normal and the nominally flat normal direction. As with the Gibbs-Thomson condition, the interfacial stiffness, defined here as $S(\theta) = \gamma + \gamma_{\theta\theta}$, inherently implies equilibrium across the interface. To introduce a temperature dependent term to the CFM, we must first look at the derivation of the system energy.

Hoyt[26] expressed the excess free energy of the two-phase system in equilibrium as $E = b \int_0^W \gamma(\theta) ds$. At the atomic scale for short time steps, the interface fluctuations are small in amplitude such that $\sqrt{1 + h'(x)^2} \approx 1 + \frac{h'(x)^2}{2}$ and $h'(x) = \tan(\theta) \approx \theta$. We can therefore redefine the energy equation with potential contributions from the temperature gradient, G as:

$$E = b \int_0^W \gamma(\theta, G) \sqrt{1 + h'(x)^2} dx \quad (2)$$

To include the effects of a one-dimensional temperature gradient, or $G = \nabla T = \frac{dT}{dh}$, on the interfacial free energy, γ , we modify Hoyt's methodology to expand the multi-variable expression through a second-order Taylor series:

$$\gamma(\theta, G) \approx \gamma + \gamma_{\theta}\theta + \gamma_G G + \frac{1}{2}(\gamma_{\theta\theta}\theta^2 + \gamma_{GG}G^2) + \gamma_{\theta G}\theta G \quad (3)$$

By substituting Equation (3) into Equation (2), we can separate the energy equation into the summation of five separate contributions along the interface, Table 1:

Under periodic boundary conditions parallel to the interface length we can reduce the second contribution term to zero, $\int_0^W h'(x) dx = 0$. Similarly under the assumption of small height fluctuations, the higher order terms of $h'(x) \approx 0$, reducing the fourth and fifth energy contributions to zero. The equation can be further simplified if we consider the first contribution to be the energy of a flat interface and define $\Delta E = E - E_1$:

$$\Delta E = \frac{1}{2}b \left(\gamma + \gamma_{\theta\theta} + \gamma_G G + \frac{\gamma_{GG}G^2}{2} \right) \int_0^W h'(x)^2 dx \quad (4)$$

If we compare Equation (4) to Hoyt's derivation for a system in equilibrium[26], $\Delta E = \frac{1}{2}b(\gamma + \gamma_{\theta\theta}) \int_0^W h'(x)^2 dx$, we notice the equations are identical when the gradient is zero and that stiffness can be defined by the term within the parenthesis:

$$S_{(\theta, G)} = \gamma + \gamma_{\theta\theta} + \gamma_G G + \frac{1}{2}\gamma_{GG}G^2 \quad (5)$$

By taking the second order expansion of the Taylor series for the interfacial free energy, an initial hypothesis is inferred that the stiffness has a power relationship with the gradient. It is possible that this relationship will be material-dependent, but will not be explored in this work. The new derivation of stiffness satisfies the boundary conditions for the equilibrium state when there is no thermal gradient, i.e. $S_{(\theta, G=0)} = \gamma + \gamma_{\theta\theta}$. By substituting the derived gradient-based interfacial stiffness into Equation (1), we can approximate a CFM equation which includes an applied temperature gradient:

$$\langle |A(k)|^2 \rangle = \frac{k_b T_{\sigma}}{bW \left(\gamma + \gamma_{\theta\theta} + \gamma_G G + \frac{1}{2}\gamma_{GG}G^2 \right) k^2} \quad (6)$$

However, this derivation assumes that all of the height fluctuations are caused by the change in interfacial stiffness which may be an oversimplification for systems in rapid solidification. From Karma's work on fluctuations in solidifications[11], we know that there are additional contributions to these fluctuations that are independent of stiffness. This was shown by deriving an equation for the fluctuation spectrum for a stationary interface in a temperature gradient:

$$\langle \xi_k \xi_{-k} \rangle_G = \frac{k_b T_\sigma}{\gamma(k^2 + a^{-2})} \quad (7)$$

where $\langle \xi_k \xi_{-k} \rangle_G$ is defined as the fluctuation spectra of a symmetric structure with a temperature gradient, $a = \sqrt{\gamma T_\sigma / LG}$, and L is equal to latent heat per unit volume. If we incorporate the quasi two-dimensional formulation of Equations (5) and (6), we can derive a solvable equation for the gradient-dependent stiffness term:

$$\langle |A(k)|^2 \rangle = \frac{k_b T_\sigma}{bW S_{(\theta, G)}(k^2 + a^{-2})} \quad (8)$$

where γ in the a term is the surface energy under equilibrium conditions. We can then calculate stiffness by plotting $\frac{k_b T_\sigma}{bW \langle |A(k)|^2 \rangle}$ versus $(k^2 + a^{-2})$ and taking the linear slot for low values of wavenumbers.

3 Methods

In this section, we define the various MD parameters and methods used in this work to calculate the interface characteristics. This includes the dimensions of the simulation model, method used to develop a two-phase state, applications of a thermal gradient, identification of the solid-liquid interface and finally, the application of the CFM to extract the interface properties.

3.1 Simulation Structure Dimensions

The interfacial free energy of aluminum is calculated using LAMMPS molecular dynamics software[28]. The geometry of the aluminum samples used for the MD simulations varies based on the lattice orientation. However, each structure meets the CFM assumptions of $b \ll W$ and the height of the structures are defined as twice the width, $H = 2W$, to limit the effects between the two interfaces and boundaries, Figure 1. As a result, the structure for each interface orientation varies in dimensions and numbers of atoms, Table 2.

An embedded-atom method (EAM) potential[29], intended for AlCu alloys, is used for the aluminum structures evaluated in this paper. The EAM potential was selected for future inclusions of copper alloy in similar calculations where the free energy may also be a function of the alloyed concentration in addition to the gradient. Unlike the more recent EAM potentials developed by Mendelev et al.[30] for the individual application of aluminum or copper, this alloy-based EAM potential was not calibrated to high temperature applications. As a result, the computed melting temperature of 750K is much less than the expected value of 933K[31]. However, the results presented in this paper focus on the change in results of non-equilibrium conditions relative to the zero-gradient equilibrium results.

3.2 Solid-Liquid Phase Structure

There are numerous methods that can create a two phase solid-liquid MD model. The one used in this work, first equilibrates the structure to the estimated melting temperature using the NVE ensemble with a fix Berendsen barostat to apply a zero external pressure condition. The temperature parameter is applied through a full-structure Langevin thermostat as the approximate melting temperature. After equilibrating for 20ps with a time step of 2fs, a new thermostat is defined in the desired liquid portion of the structure, and the temperature is first increased by 500K for 50ps and then cooled back to the melting temperature. The temperature, applied through the full structure thermostat, is held until an equilibrated state is reached, approximately 1ns in these simulations. During the equilibration step, the interface between solid and liquid phases is observed to verify no translational movement and that the assumed melting temperature is accurate. With the melting temperature verified, the Langevin thermostat is removed and the structure is equilibrated first using only the Berendsen barostat for 200ps. Finally, the pressure barostat is removed, leaving only the NVE ensemble, and is run for an additional 200ps. This method creates a stable solid-liquid interface under thermal equilibrium conditions, Figure 2, for general applications of material selection.

3.3 Application of Thermal Gradients

With a stable two-phase structure in thermal equilibrium at the melting temperature, we can define a method to apply thermal gradients while maintaining a stationary interface. The method devised for this work applies a Langevin thermostat, 20 angstroms thick, to the center of each phase, with an NVE ensemble applied to the remaining portions of the model, Figure 3. These thermostats are defined as dynamic regions, meaning the atoms in the system are allowed to move freely in and out of the area without restrictions. The size of the thermostats is kept to a small portion of the model to reduce any unwanted influence on the interface, verified through the post processed temperature profile at the end of the equilibration. After ramping the Langevin thermostats to the desired temperatures over 200ps, and with an applied zero external pressure boundary condition, the simulation is again equilibrated with the new temperature profile for an additional 200ps. Finally, the simulation is run for an additional 400ps with a snapshot of the atom positions at every 0.2ps resulting in 1,000 snapshots of the atomic structure, used for the application of the CFM.

To calculate what temperatures the thermostats should be to get the desired temperature gradients, it is helpful to look at the application of Fourier's law for the conservation of heat flux across the interface:

$$\frac{1}{z_L} \int_{T_m}^{T_L} \kappa_L dT = \frac{2}{z_S} \int_{T_S}^{T_m} \kappa_S dT \quad (9)$$

While we are working with a constant material for both phases, the use of a temperature gradient as well as two phases results in a non-linear conductivity, $\kappa(T)$, along the temperature profile, Figure 3. In MD simulations, the thermal conductivity can be calculated for a material given a specific temperature by first calculating the heat flux of the system and then relating it to the conductivity term through the Green-Kubo formulas. This method was used to create two functions, κ_L and κ_S , for the two phases of the structure. Then, using the location of the interfaces at equilibrium, we can define a desired temperature gradient and calculate the

temperatures for the two thermostats. In this paper, we are interested in a range of gradients, approximately from 11~35 K/nm, to develop a trend in the interfacial characteristics. Since the dimensions of the structures vary based on the interface orientation, Table 2, to maintain the comparable gradients, the calculation of thermostat temperatures must account variations in height and location of the equilibrium interface. The resulting calculations of thermostat temperatures have been provided in Table 3 for reference.

3.4 Defining the Solid-Liquid Interface

To identify the location of the interface, a centrosymmetry parameter for FCC structures, $P = \sum_{i=1}^6 |\vec{r}_i + \vec{r}_{i+6}|^2$, is assigned for each atom, i , where $\vec{r}$ is used to indicate the vector position of the nearest neighbors. During the simulation, each structure is partitioned into a mesh for collecting the mean centrosymmetry parameter per bin. The size of the bins along the x-axis contribute to how detailed the interface is defined. For consistency across the model sizes, the bin size (X x Y) defined for this work is 4.050 x 2.025 angstroms. With the average parameter calculated, we can create height profiles perpendicular to the interface and plot the results of the mean centrosymmetry parameters per bin, Figure 4. We define the interface as the maximum difference in centrosymmetry between a region above and below the specified height point. This process is repeated along the interface length to develop an interface height profile, $h(x)$, for each snapshot, which is then used for the CFM.

3.5 CFM and Anisotropy

Through the derivation outlined in Section 2 of this paper, we know that interfacial stiffness can be connected to the fluctuation in interface height through Equations (5) and (6) where $h(x) = \sum_k A(k)e^{ikx}$. The interfacial stiffness can then be extracted from a linearly proportional relationship between $\frac{k_b T_\sigma}{bW \langle |A(k)|^2 \rangle}$ versus $(k^2 + a^{-2})$. In addition, Hoyt et. al.[25] have shown for the weakly anisotropic crystal nature of solid-liquid interfaces, the interfacial free energy can be obtained as a function of the interface normal, $\gamma(\hat{n})$. This term can be expanded through cubic harmonics[27, 31, 32] such that:

$$\frac{\gamma(\hat{n})}{\gamma_0} = 1 + \delta_1 \left(\sum_{i=1}^3 n_i^4 - \frac{3}{5} \right) + \delta_2 \left(3 \sum_{i=1}^3 n_i^6 + 66n_1^2 n_2^2 n_3^2 - \frac{17}{7} \right) \quad (10)$$

where n_i are the components of the interface normal $\hat{n}$ in the Cartesian coordinate system (x_1, x_2, x_3). δ_1 and δ_2 are related to the parameters for surface anisotropy. For quasi-2D structures, where the thickness is negligible, the interface normal can be defined as:

$$n_i = [\sin(\theta)\hat{x}_1 + \cos(\theta)\hat{x}_3]\hat{z}_i, \quad i = 1, 2, 3 \quad (11)$$

$$\hat{x}_i = \frac{a_i \hat{z}_1 + b_i \hat{z}_2 + c_i \hat{z}_3}{\sqrt{a_i^2 + b_i^2 + c_i^2}} \quad (12)$$

where $\hat{z}_i$ is equal the unit vectors [100], [010], and [001] and the a_i, b_i, c_i terms are used to define the interface orientation. Under the assumption that the anisotropic characteristics of the solid-liquid interface are independent of thermal conditions, we can derive equations for the various orientations at equilibrium that satisfy $\gamma + \gamma_{\theta\theta}|_{\theta=0}$, Table 4. Theoretically, with the

selection of three discrete orientations, we can calculate an interfacial energy along with the ϵ and δ anisotropic parameters. For verification, we look at a total of six interface orientations. In the following section, we calculate the interface material properties for an aluminum solid-liquid interface in thermal non-equilibrium and develop a trend for use in interpolation. In addition to the calculation of interfacial stiffness and energy, we test the hypothesis that the anisotropy parameters, δ_1 and δ_2 , are independent variables of the applied gradient.

4 Results and Discussion

In this section, the interfacial stiffness of aluminum is calculated for six lattice configurations, Table 2, and used to determine the anisotropic characteristics. More specifically, the solid-liquid MD simulations are initially run at the melting temperature, and then with approximate gradients of 12, 23 and 34 K/nm to identify gradient-dependent behaviors. An interfacial energy per temperature gradient relationship is identified and verified against the presented theory in Section 2. Finally, we check the assumption that material anisotropy is independent of the gradient by calculating the interfacial energy using the equilibrium anisotropy parameters compared to the temperature gradient specific parameters.

As a control, the interfacial stiffness is initially calculated at thermal equilibrium when the temperature of the system is set to the melting temperature for the EAM potential, 750K, for aluminum. The latent heat per unit volume, L , used for aluminum is approximated as $867 \frac{\text{mJ}}{\text{cm}^3}$ and is used to calculate the stiffness-independent fluctuation contribution, Equation (8). The stiffness is defined as the average of the two interfaces for each orientation. The stiffness values for the 100[010], 110[001], and 110[$\bar{1}10$] orientations are used to calculate interfacial free energy and the anisotropy parameters resulting in: $\gamma_0 = 53.3 \text{ mJ/m}^2$, $\delta_1 = 5.54\%$ and $\delta_2 = -0.10\%$. The expected interfacial energy of aluminum is in the range of 140~170mJ/m² based on experimental data and well fitted EAM and MEAM potentials[31]. Given the large discrepancy in melting temperature for the selected potential, as described in Section 3.1, the poor representation of interfacial energy at equilibrium is not surprising. These results highlight the need for controlled simulations to be used for reference in MD simulations. When the parameters are verified against the other three orientations, the stiffness can be predicted within 8% of the calculated value, which is within the typical spread for this CFM method for results using one random seed number. Following the same procedure, the stiffness is calculated for each temperature gradient in each orientation and the results of the 100[010], 110[$\bar{1}12$], and 110[$\bar{1}10$] orientations, Figure 5, are again used to calculate temperature-dependent properties. It should be noted that when $G \neq 0$, the x-intercept should be located at a^{-2} rather than zero, as it is for the standard equilibrium case.

Under the assumption that the anisotropy of the solid-liquid interface is independent of thermal gradient, we can use the δ_1 and δ_2 parameters, calculated under equilibrium conditions, to calculate the interfacial free energy for each orientation using the equations in Table 4. Averaging the interfacial energy of the orientations results in a linear interfacial energy-temperature gradient relationship, Figure 6. To verify the assumption of temperature gradient independence for material anisotropy, we repeat the steps of equilibrium to calculate the gradient-dependent parameters, Figure 7. From the plot of anisotropy parameters, there appears to be no correlation between anisotropy and temperature gradient. To verify, the interfacial energies are calculated using the three orientations and the new gradient-dependent anisotropy, Figure 6. Comparing the

interfacial energies calculated from the gradient dependent and independent anisotropies, it is confirmed that there is negligible impact due to the applied gradient.

From the plot of interfacial free energy versus temperature-gradient, an energy function for aluminum can be identified as $\gamma_{(\theta,G)} = \mu G + \gamma_o$, where $\mu = 0.746 \frac{\text{mJ} \cdot \text{nm}}{\text{m}^2 \text{K}}$ and γ_o is equal to the interfacial free energy at thermal equilibrium. Returning to the hypothesis that interfacial stiffness can be derived from a second order Taylor expansion of the interfacial energy, Equation (5), we see that the higher order term can be dropped in the case of pure aluminum where the energy-gradient relationship is linear. Therefore, the solid-liquid interfacial stiffness for aluminum can be theoretically defined as $S_{(\theta,G)} = \gamma + \gamma_{\theta\theta} + \mu G$, and compared to the MD simulation calculations, Figure 8. The error bars, shown in the figure, provide the deviation between the interfacial stiffness calculated between the two interfaces in the structure. The MD results show good agreement with the hypothesized theory confirming the assumptions of gradient-independent anisotropy parameters and first order Taylor expansion of interfacial energy. With additional sampling of random seed numbers, the gap between theory and simulations is expected to close further.

5 Conclusions

MD simulations are performed for applications in CFM on a solid-liquid interface of pure aluminum. The interfacial properties of energy, stiffness and anisotropy are calculated under thermal equilibrium and non-equilibrium conditions seen in rapid solidification processes, such as additive manufacturing. The application of a temperature gradient across the interface results in increased stiffness and energy properties while retaining anisotropy characteristics. These increased parameters can be theoretically explained through a multi-variable Taylor expansion of interfacial free energy and the derivation of the system energy at the solid-liquid interface. The resulting energy and stiffness equations are $\gamma_{(\theta,G)} = \mu G + \gamma_o$ and $S_{(\theta,G)} = \gamma + \gamma_{\theta\theta} + \mu G$ respectively. For the EAM modeled aluminum presented in this work, $\mu = 0.746 \frac{\text{mJ} \cdot \text{nm}}{\text{m}^2 \text{K}}$ and $\gamma_o = 53.3 \text{ mJ/m}^2$. While published sources state typical gradients for additive manufacturing processes to be on the range of $10^3 \sim 10^5 \text{ K/mm}$ [12, 19], these numbers are estimated at larger scales through finite element analysis(FEA) approaches and may not accurately represent the gradient across the interface at an atomic scale. MD simulations are limited in size to a length scale on the order of nanometers which in turn limits the applied temperature gradient. Regardless, the work presented develops a temperature gradient-stiffness and energy relationship which can be interpolated for additional computational applications.

The results conclude that the solid-liquid interface properties can be influenced by a temperature gradient across the interface, replicating a rapid solidification system. Consequently, the dendrite growth phase-field simulations that rely on the application of the Gibbs-Thomson condition to determine the temperature at the interface, may be inaccurately assuming equilibrium conditions for systems of extreme heating and cooling rates. As a result, it may be a contributing factor to the poor phase-field geometric representations at high interface velocities. By incorporating the non-equilibrium thermal conditions into the multi-scale computational methods, we can begin to close the gap between experimental inconsistency in material strength and the predicted computational results. Additional factors remaining and the future work

includes a correlation study of: the temperature at the interface deviating from the melting temperature and the composition concentration defined in metal-alloys in connection with the temperature gradient studied in this work.

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7 References

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Interfacial Stiffness and Free Energy Dependent on Temperature Gradient

Table 1: Approximate energy contributions at an interface with applied temperature gradient

$E:$	$b \int_0^W \gamma(\theta, G) \sqrt{1 + h'(x)^2} dx = \sum_{i=1}^5 E_i$
$E_1:$	$b \int_0^W \left[\gamma + \gamma_G + \frac{\gamma_{GG} G^2}{2} \right] dx$
$E_2:$	$b \int_0^W h'(x) [\gamma_\theta + \gamma_{\theta G} G] dx = 0$
$E_3:$	$b \int_0^W h'(x)^2 \left[\frac{\gamma}{2} + \frac{\gamma_{\theta\theta}}{2} + \frac{\gamma_G G}{2} + \frac{\gamma_{GG} G^2}{4} \right] dx$
$E_4:$	$b \int_0^W h'(x)^3 \left[\frac{\gamma_\theta}{2} + \frac{\gamma_{\theta G} G}{2} \right] dx = 0$
$E_5:$	$b \int_0^W h'(x)^4 \left[\frac{\gamma_{\theta\theta}}{4} \right] dx = 0$

Table 2: Simulation sizes for six interface orientations

Orientation*	Atoms	H (Å)	W (Å)	b (Å)
100[010]	204,800	680	332	17
100[012]	460,800	682	446	28
110[001]	409,600	963	333	23
110[1 $\bar{1}$ 0]	409,600	962	469	17
110[1 $\bar{1}$ 2]	460,800	723	407	29
110[$\bar{1}$ 10]	409,600	962	469	17

*The first number of the notation indicates the direction perpendicular to the interface, the number in brackets denotes the direction along the interface length.

Table 3: Temperature gradient and thermostat definitions.

Orientation	G (K/nm)	T _L (K)	T _S (K)	T _σ [*] (K)
100[010]	11.8	1002	594	764
	23.3	1308	492	808
	34.2	1649	425	871
100[012]	11.8	1009	600	771
	23.3	1320	502	818
	34.2	1665	438	882
110[001]	11.8	1131	553	782
	23.0	1602	446	849
	33.2	2118	384	931
110[1 $\bar{1}$ 0]	11.8	1130	553	780
	23.0	1599	445	847
	33.2	2113	382	931
110[1 $\bar{1}$ 2]	11.8	1027	593	774
	23.2	1362	494	826
	34.0	1731	430	898
110[$\bar{1}$ 10]	11.8	1133	556	784
	22.9	1603	449	852
	33.2	2118	387	935
* Mean temperature of the system. Term used for the CFM calculation of interface properties.				

Table 4: Anisotropy for multiple interface orientations

Orientation	$\frac{\gamma + \gamma_{\theta\theta} _{\theta=0}}{\gamma_0}$
100[010]	$1 - \frac{18}{5}\delta_1 - \frac{80}{7}\delta_2$
100[012]	$1 - \frac{18}{5}\delta_1 - \frac{80}{7}\delta_2$
110[001]	$1 - \frac{21}{10}\delta_1 + \frac{365}{14}\delta_2$
110[1 $\bar{1}$ 0]	$1 - \frac{39}{10}\delta_1 + \frac{155}{14}\delta_2$
110[1 $\bar{1}$ 2]	$1 - \frac{1}{10}\delta_1 + \frac{295}{14}\delta_2$
110[$\bar{1}$ 10]	$1 - \frac{39}{10}\delta_1 + \frac{155}{14}\delta_2$

Figure 1. Quasi-2D model of $100[010]$ orientation of solid-liquid simulation model for pure aluminum

Figure 2. Atomic structure of a system in a two-phase state consisting of an amorphous liquid and crystalline solid. Interface graphically defined as the boundary between the two phases.

Figure 3. Applied thermostats to a solid-liquid structure of aluminum. Temperature is sampled along the width of the structure for every height and averaged to verify temperature profile.

Figure 4. Atomic structure of a structure in a two-phase state consisting of an amorphous liquid and crystalline solid. Interface graphically defined as the boundary between the two phases.

Figure 5. CFM for aluminum solid-liquid interface, plots of $k_B T_m / bW \langle |A(k)|^2 \rangle$ versus $k^2 + a^{-2}$ to calculated interfacial stiffness at equilibrium and three temperature gradients. (a) 100[010] orientation (b) 110[112] orientation (c) 110[110] orientation.

Figure 6. Interfacial free energy of aluminum solid-liquid interface under various temperature gradients. Verification of the assumption of thermal-gradient independence for anisotropy parameters.

Figure 7. Temperature gradient versus anisotropy parameters for aluminum.

110[$\bar{1}10$]

Figure 8. Interfacial stiffness of 110[$\bar{1}10$] interface orientation. Calculated MD results compared to theoretical equation.