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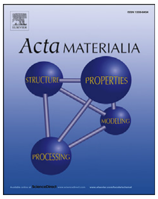

Full length article

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 to 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.

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-

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Thomson condition, often supplemented 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 the equilibrium 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 interface properties, 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 can develop material specific temperature gradient-dependent relationships 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 stiffness is often calculated using the capillary fluctuation method (CFM) [25–27] on a thin quasi-2D system. This method relates the interfacial stiffness to the mean square amplitude, $h(x) = \sum_k A(k)e^{ikx}$, through equipartition and Fourier mode analysis such that:

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

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:

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

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:

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

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 $\Delta E = E - E_1$:

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

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:

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

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

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:	$b\int_0^W h'(x)^4\left[\frac{\gamma_{\theta\theta}}{4}\right]dx = 0$