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Calculation of alloy solid-liquid interfacial free energies from atomic-scale simulations

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Solid-liquid interfacial free energies and associated crystalline anisotropies are calculated for a model Ni-Cu alloy system based upon the analysis of equilibrium capillary fluctuations in molecular-dynamics simulations. Alloying of Ni by Cu leads to a reduction in the magnitude of the calculated interfacial free energy, while having only a minor effect on computed anisotropies. The present study demonstrates the viability of applying the fluctuation method to simulation-based calculations of solid-liquid interfacial free energies in alloys.

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The solid-liquid interfacial free energy (γ) is a critical factor influencing transformation rates and microstructural morphologies accompanying crystal growth from the melt. Due to significant challenges associated with direct experimental measurements of solid-liquid interface properties, a growing number of molecular-dynamics (MD) studies have been undertaken to compute both the magnitude of γ and the strength of its crystalline anisotropy. To date these simulation studies have focused on elemental systems, as modeled by hard-sphere, Lennard-Jones, and embedded-atom-method (EAM) interatomic potentials,[1–6] and use has been made of two distinct MD methods for calculating the interfacial free energy. In the thermodynamic-integration approach pioneered by Broughton and Gilmer,[1] externally imposed ‘‘cleaving potentials’’ are employed in the calculation of the reversible work to form a crystal-melt interface from isolated bulk solid and liquid phases.[1–3] Recently, Hoyt *et al.*[4] demonstrated an alternative approach for the calculation of γ from an analysis of equilibrium capillary fluctuations in MD simulations for molecularly rough solid-liquid interfaces.

As discussed in detail previously,[4–6] a relative advantage of the fluctuation method is that it measures the interface *stiffness* which is an order of magnitude more anisotropic than γ itself. Consequently, this technique provides an effective approach for calculating anisotropies in γ that are typically small (on the order of 1–2 %) for rough interfaces, yet which are of critical importance for selecting the steady-state operating point of a dendrite tip during solidification.[7–9] In the present study we demonstrate an additional application of the fluctuation approach in the calculation of solid-liquid interfacial free energies for binary *alloys*. Simulation studies have played a critical role in developing a microscopic understanding of the equilibrium properties of solid-liquid interfaces in elemental systems.[10] However, far fewer related studies have been undertaken to date for mixtures.[11–13] In particular, the effects of alloying upon the magnitude and anisotropy of the solid-liquid interfacial free energy remain unstudied by atomic-scale simulations.

As described in detail in Ref. 4, the fluctuation method for calculating solid-liquid interfacial free energies is based upon the following expression for the equilibrium fluctuation spectrum of a quasi-one-dimensional interface:

$$\langle |A(k)|^2 \rangle = \frac{k_B T}{bW(\gamma+\gamma'')k^2}, \tag{1}$$

where $A(k)$ is the Fourier transform of the interface height profile and angular brackets correspond to equilibrium values. W and b, with $b \ll W$, denote the length and thickness of the solid-liquid boundary, and $k_B T$ is Boltzmann's constant times the temperature. The term $\gamma+\gamma''$ corresponds to the interface stiffness, where γ'' is the second derivative of γ as a function of the angle of the local interface normal relative to its average orientation. Equation (1) applies equally to solid-liquid interfaces in alloys and pure elements, and the fluctuation method therefore provides a natural strategy for simulation-based calculations of interfacial free energies for binary systems. In extending the method to mixtures, however, an important consideration is the coupling betweeen interface fluctuations and the solute concentration field, leading to increased fluctuation relaxation times in alloys relative to pure elements. Slower relaxation rates imply a need for longer simulation times to achieve comparable statistical accuracy in sampling of the fluctuation spectra.

Below we present results applying the fluctuation method to the calculation of interfacial free energies for a prototypical metallic alloy system, Ni-Cu. We demonstrate statistical accuracies for interfacial free energies and associated crystalline anisotropies on the order of 5% and 15%, respectively, employing MD simulations with moderate lengths of 0.5–1 ns. A theoretical analysis based upon the Langevin formalism of Ref. 14 is presented, suggesting that such simulation times should be generally sufficient to achieve comparable statistical accuracies in fluctuation-based calculations of interfacial free energies for a broad class of alloy systems. The present results therefore establish the fluctuation method as a viable approach to simulation-based calculations of anisotropic solid-liquid interfacial free energies in alloys.

Simulation cells with coexisting solid and liquid alloy phases were equilibrated employing a combination of molecular-dynamics and Monte Carlo simulation methods. As described in detail elsewhere,[13] the initial step is a computation of the equilibrium solidus and liquidus phase boundaries through thermodynamic-integration calculations of bulk-alloy free energies. The present study focuses on

TABLE I. Calculated stiffness values ($\gamma+\gamma''$) as a function of interface orientation for a Ni-Cu alloy. Error bars respresent estimated 95% confidence levels associated with statistical sampling.

Orientation	$(\gamma+\gamma'')/\gamma_0$	$\gamma+\gamma''$ (mJ/m^2)
100 [0$\underline{1}$0]	$1-\frac{18}{5}\epsilon_1-\frac{80}{7}\epsilon_2$	224±8
110 [$\bar{1}$10]	$1+\frac{39}{10}\epsilon_1+\frac{155}{14}\epsilon_2$	331±14
110 [001]	$1-\frac{21}{10}\epsilon_1+\frac{365}{14}\epsilon_2$	175±10

Ni-rich Ni-Cu alloys employing EAM interatomic potentials developed previously by Foiles.[15] Calculated solid-liquid phase boundaries derived from these potentials are given in Ref. 13. The Foiles potentials are found to overestimate the melting point for pure Ni by roughly 100 K (1820±6 K calculated vs 1728 K measured), although the equilibrium partition coefficient (i.e., the ratio of the equilibrium solidus and liquidus solute compositions) is in reasonable agreement with experimental measurements (0.5±0.05 calculated vs roughly 0.6 measured). Since the primary focus of the work presented here is to extend the fluctuation approach to calculations of solid-liquid interfacial free energies in alloys, no effort was devoted to refine the EAM potentials for Ni-Cu in the present study.

Periodic simulation cells with coexisting solid and liquid alloy phases were prepared at a temperature of 1750 K (96% of the melting temperature calculated for pure Ni) following the approach described in Ref. 13. In the bottom and top halves of a pure Ni sample, Cu solute was randomly substituted to establish the equilibrium solidus and liquidus compositions of 5.0 and 10.4 at. % Cu, respectively, derived from the thermodynamic-integration calculations.[13] Subsequently, the liquid half was melted in Monte Carlo simulations at high temperature, keeping the atomic positions in the remainder of the cell fixed. Next, density and composition profiles were equilibrated employing semi-grand-canonical[15] Monte Carlo simulations. In these simulations, sampling was performed over atomic displacements as well as compositional degrees of freedom, the latter being performed through Monte Carlo steps involving changes in chemical identities with an imposed chemical potential difference between Ni and Cu corresponding to two-phase solid-liquid equilibrium (as derived from the calculated bulk free energies). The dimensions of the cell parallel to the solid-liquid interfaces were constrained at values dictated by the zero-stress lattice constant of the crystalline phase at its equilibrium solidus composition, while the periodic length normal to the interface was adjusted to minimize the overall stress.

Three quasi-two-dimensional simulation cells, corresponding to different orientations of the solid-liquid interface, were prepared in this manner. The orientations for each of these cells are listed in Table I following the notation of Ref. 4, where the first set of numbers specifies the interface normal, while the numbers in brackets give the direction of the long axis parallel to the interface. The cell dimensions W and b were chosen with values comparable to those employed in previous calculations for pure elements:[4,5] $W=232.7$ Å for 100[010] and 110[001], and 246.82 Å for 110[110]; $b=10.91$ Å for 100[010] and 110[110], and 10.28 Å for 110[001]. The length of the cells normal to the solid-liquid interfaces was roughly $2W$, and each cell contained on the order of 10^5 atoms.

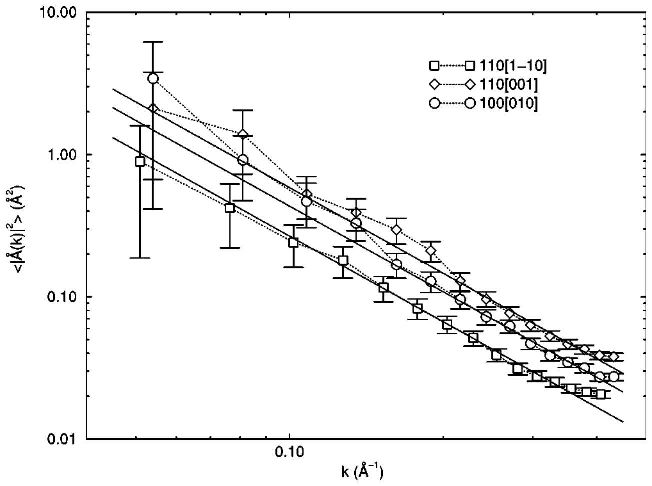

FIG. 1. Equilibrium fluctuation spectra $\langle|A(k)|^2\rangle$ derived from MD simulations for a Ni-Cu alloy are plotted on a log-log scale vs wavelength k. Solid lines indicate the theoretical slope of k^{-2}. Error bars represent estimated standard statistical uncertainties.

Subsequent to equilibration by Monte Carlo, the resulting interface simulation cells were used as the starting point in molecular-dynamics simulations to measure interface capillary fluctuations. MD simulations were performed in a microcanonical ensemble employing a time step of 0.002 ps. After equilibration periods lasting on the order of 10^5 time steps, interface configuations were sampled in simulations lasting roughly 600 ps. During these simulations the height vs lateral position of the two solid-liquid interfaces was extracted every 100 time steps, and the resulting data was used to compute the Fourier amplitudes $A(k)$ appearing in Eq. (1). The method used to distinguish between solid and liquid atoms and the procedure for identifying the interface boundary were the same as those employed in previous studies for pure elements.[4]

Figure 1 plots on a log-log scale values of $\langle|A(k)|^2\rangle$ versus wave number derived from the MD simulations. Error bars represent standard statistical uncertainties, estimated according to the following formula for the variance in the mean value of $\langle|A(k)|^2\rangle$, derived from the property that $A(k,t)$ obeys Gaussian statistics (e.g., Ref. 16): $\sigma^2 = 2\langle|A(k)|^2\rangle^2\tau(k)/t_{run}$. The relaxation times $\tau(k)$ were calculated by integrating time correlation functions $\langle A(k,t)A(-k,0)\rangle^2/\langle|A(k)|^2\rangle^2$ derived from the MD data. The solid lines through each set of data in Fig. 1 correspond to the theoretical slope of -2 given by Eq. (1). For each interface orientation the predicted slope is observed to hold to within the estimated statistical accuracy of the MD data for small and intermediate values of k. At the highest wave numbers the fluctuation wavelengths approach atomic dimensions and the observed deviations from the predictions of Eq. (1) are expected. In deriving stiffness values from the MD data, we performed a least-squares fit of $k_BT/[bW\langle|A(k)|^2\rangle]$ vs k^2, as shown in Fig. 2, using the data for values of k ranging between 0.05 and 0.38 Å^{-1}, thereby excluding data for the

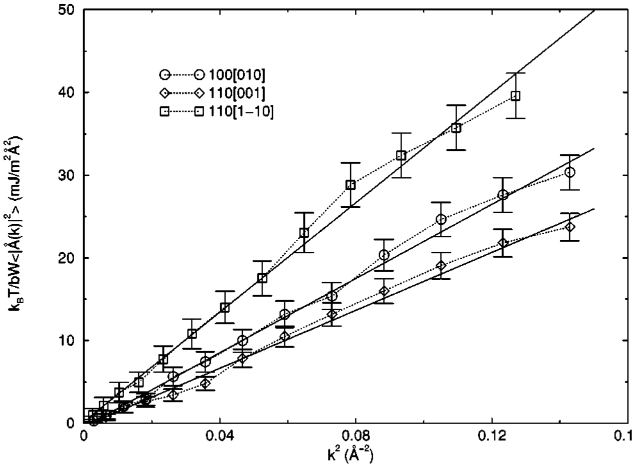

FIG. 2. $k_BT/bW\langle|A(k)|^2\rangle$ vs k^2 for a Ni-Cu alloy calculated at 1750 K. The solid lines represent the least-squares fit for each orientation. Interface stiffness values reported in Table I correspond to the slopes of these best-fit lines.

two highest wave numbers for each orientation. The resulting values of $\gamma+\gamma''$ for each interface orientation are listed in Table I.

The interfacial free energy and its associated anisotropy can be derived from the results given in Table I through the use of an expansion of $\gamma(\hat{n})$ in terms of cubic harmonics, i.e., linear combinations of spherical harmonics that obey the cubic crystalline symmetry. In previous studies for elemental Ni (Ref. 4) and Al,[6] it was found that the anisotropy of γ can be accurately parametrized using the fourth- and sixth-order terms of a so-called ‘‘Kubic-Harmonic’’ expansion.[17] In the present study we employ an equivalent form for the cubic-harmonic expansion proposed by Fehlner and Vosko[18] in studies of Fermi surfaces in metals,

$$\gamma(\hat{n})/\gamma_0 = 1+\epsilon_1\left(\sum_{i=1}^{3} n_i^4-\frac{3}{5}\right) + \epsilon_2\left(3\sum_{i=1}^{3} n_i^4+66n_1^2n_2^2n_3^2-\frac{17}{7}\right), \tag{2}$$

where $\hat{n}=(n_1,n_2,n_3)$ is the interface normal. We prefer the Fehlner and Vosko formulation owing to the desirable property that all the terms in the expansion are orthogonal to each other when integrated over the unit sphere. Orientation-dependent expressions for the interface stiffness in terms of the anisotropy parameters in Eq. (2) are given in Table I. From these expressions and the stiffness values derived from the MD fluctuation spectra, we obtain the values of γ_0, ϵ_1, and ϵ_2 for the Ni-Cu alloy listed in Table II. Also given in Table II are values of the average interfacial free energy and associated anisotropy parameters computed for elemental Ni employing MD simulations based upon the same Foiles EAM potentials used in the alloy calculations. The interfacial free energy anisotropies $[(\gamma_{100}-\gamma_{110})/2\gamma_0$ and $(\gamma_{111}-\gamma_{110})/2\gamma_0]$ listed in Table II are on the order of a few percent and are comparable to values derived from previous calculations[4–6] and recent experimental measurements[19] for metallic systems. From a comparison of the results in Table II, it can be seen that alloying leads to a reduction in the magnitude of the calculated solid-liquid interfacial free energies, while no statistically significant changes in anisotropy are found.

TABLE II. Calculated values of the average solid-liquid interfacial free energy and associated crystalline anisotropies for elemental Ni and a Ni-Cu alloy as derived from MD simulations based on the EAM potentials of Foiles (Ref. 15). Error bars represent estimated 95% confidence levels.

	γ_0	ϵ_1	ϵ_2	$\frac{\gamma_{100}-\gamma_{110}}{2\gamma_0}$	$\frac{\gamma_{100}-\gamma_{111}}{2\gamma_0}$
	(mJ/m^2)	(%)	(%)	(%)	(%)
Ni-Cu	287±8	7.2±0.8	−0.7±0.1	1.2±0.2	2.5±0.4
Ni	310±7	9.0±0.6	−1.1±0.1	1.4±0.2	3.2±0.5

The results in Table II demonstrate statistical accuracies on the order of 5% and 15% for calculated alloy solid-liquid interfacial free energies and crystalline anisotropy parameters, respectively. As described above, the statistical accuracy in an MD calculation of $\langle|A(k)|^2\rangle$ is dictated by the length of the simulation relative to the interface relaxation time $\tau(k)$. For the Ni-Cu alloy considered in the present study, calculated values of $\tau(k)$ vary between roughly 1 and 150 ps for fluctuation wavelengths ranging between 16 and 80 Å. These values are consistent with a k^{-3} dependence for $\tau(k)$ expected in the limit that dynamic interface fluctuations are limited by solute diffusion. Namely, with only solute diffusion, the amplitude of a linear perturbation of the interface of wavelength $\lambda=2\pi/k$ relaxes exponentially in time (i.e., $\sim e^{-t/\tau(k)}$) with

$$\tau(k)=\frac{|m|(x_L^0-x_S^0)}{D_L\Gamma k^3}, \tag{3}$$

where $\Gamma=(\gamma+\gamma'')T_M/L$ is the Gibbs-Thomson coefficient for the solvent, L is the latent heat of melting, D_L is the solute diffusivity in the liquid, m is the liquidus slope, and $(x_L^0-x_S^0)$ gives the difference between bulk equilibrium liquid and solid compositions. This expression can easily be obtained from the Mullins-Sekerka[20] stability spectrum in the limit of an isothermal alloy (i.e., with no thermal gradient) at zero growth rate. In contrast, with only interface kinetics, exponential relaxation occurs with a time constant[14]

$$\tau(k)=\frac{1}{\mu\Gamma k^2}, \tag{4}$$

where μ is the interface kinetic coefficient. Owing to the different powers of k in the two above expressions for $\tau(k)$, the largest relaxation time of a fluctuation of wavelength λ is governed by diffusion and interface kinetics for $\lambda\gg\lambda^*$ and $\lambda\ll\lambda^*$, respectively, where the crossover wavelength $\lambda^*=2\pi/k^*=2\pi D_L/[\mu|m|(x_L^0-x_S^0)]$ is readily obtained by finding the k^* for which the two expressions for $\tau(k)$ are equal. The same result can be obtained more formally by extending to isothermal binary alloys the Langevin formalism developed previously for pure melts.[14] This formalism also makes it possible to calculate an explicit expression for the dynamic correlation function $\langle A(k,t)A(-k,0)\rangle$ with both interface kinetics and diffusion present. This expression generally depends on both μ and D_L, suggesting that the formalism could be employed to extract μ from MD-derived interface-fluctuation spectra for alloys, with D_L computed independently from the standard Green-Kubo formalism.[22]

For the Cu-Ni alloy considered in the present study, we compute $D_L=0.4\times10^{-4}$ cm^2/s, and a value of $\mu=50$ cm/s K can be estimated based upon previous calculations of the kinetic coefficient for related systems.[5] From these kinetic parameters, and the thermodynamic properties quoted above, we derive a crossover wavelength of $\lambda^*\approx16$ Å. Hence, the relaxation of dynamic interface fluctuations is predicted to be predominantly controlled by solute diffusion in the liquid over the entire range of wavelengths probed in the MD simulations. From Eq. (3), values of τ are predicted for the Ni-Cu alloy considered in this study, ranging from 0.7 to 170 ps in the range of λ between 16 and 80 Å, in good agreement with the values derived directly from MD.

The results of the present study suggest that the capillary fluctuation method should be broadly applicable in the calculation of interfacial free energies for molecularly rough solid-liquid interfaces in metallic alloys. Specifically, Eq. (1) represents a general relation between capillary fluctuation amplitudes and interfacial stiffness, valid for systems with an arbitrary number of elemental constituents. The practical application of the capillary fluctuation method, however, relies on the ability to accurately sample fluctuation spectra over reasonable simulation time scales. In Eq. (3), γ/L is known to be roughly constant for simple metals,[21] and D_L is of the same order of magnitude for many liquid alloy systems. Equation (3) therefore suggests that the relaxation times for interface fluctuations will be generally of the same order of magnitude as those derived here for Ni-Cu. The fluctuation method is thus expected to provide statistical accuracies comparable to those demonstrated in the present study for a wide range of metallic-alloy systems.

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