Method for Computing Short-Range Forces between Solid-Liquid Interfaces driving Grain Boundary Premelting

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We present a molecular dynamics based method for computing accurately short-range structural forces resulting from the overlap of spatially diffuse solid-liquid interfaces at wetted grain boundaries close to the melting point. The method is based on monitoring the fluctuations of the liquid layer width at different temperatures to extract the excess interfacial free-energy as a function of this width. The method is illustrated for a high energy Σ9 twist boundary in pure Ni. The short-range repulsion driving premelting is found to be dominant in comparison to long-range dispersion and entropic forces and consistent with previous experimental findings that nanometer-scale layer widths may only be observed very close to the melting point.

The term premelting refers to the formation of a thin, thermodynamically stable, liquid-like film at an interface for temperatures below the equilibrium melting point (T_M). Premelting at grain boundaries (GB) can have dramatic consequences in the context of materials processing, and the physical properties of polycrystals at high homologous temperatures. Despite the importance of this phenomenon, direct experimental observations of GB premelting remain relatively rare, particularly in the case of pure materials [2, 3]. Consequently, outstanding fundamental questions remain concerning the nature of the forces which drive premelting at these internal interfaces. In this Letter we introduce a molecular dynamics (MD) method that exploits large fluctuations in GB width to compute short-range forces resulting from the overlap of spatially diffuse crystal-melt interfaces from two grains of different orientations. We demonstrate the application of this method in a direct calculation of the excess free-energy of the GB as a function of this width for a high-energy boundary in a classical model of elemental Ni. The results yield quantitative insights into the relative magnitudes of these short-range structural forces and other long-ranged contributions, and help explain the origins of the experimental observations [2] that GB premelting in pure metals may occur only over extremely small temperature ranges near T_M.

Premelting generally reflects a competition between opposing bulk and interfacial thermodynamic factors, giving rise to a free energy (per unit area) of the following form (e.g., [4]):

\[ G(w) = \Delta G_f w + \Psi(w). \]  (1)

In Eq. 1 w represents the width of the premelted layer, ΔG_f is the free energy difference between solid and liquid (per unit volume) that penalizes the formation of liquid films below T_M, and Ψ(w) is the so-called “disjoining potential” which takes the limits of γ_GB (the interfacial free energy of a “dry” grain boundary) and 2γ_SL (twice the solid-liquid interfacial free energy) for zero and infinite w, respectively. In general, the disjoining potential contains both repulsive and attractive contributions. Long-ranged dispersion forces lead to an attractive interaction between solid-liquid interfaces [4, 5] which are dominant at large w and are predicted to give rise to finite interfacial widths at T_M [4]. For ΔG = γ_GB − 2γ_SL > 0, a repulsive contribution to Ψ(r) arises from short-ranged structural interactions (Ψ_sr), associated with the overlap of the diffuse regions of the solid-liquid interfaces. The exact nature of this structural contribution remains less well understood.

Mean-field arguments [6], as well as lattice-gas models (e.g., [7]), yield an exponentially decaying form for the short-ranged contribution to the disjoining potential:

\[ \Psi_{sr}(w) = 2γ_{sl} + \Delta \gamma \exp[-w/\delta] \]  (2)

where δ is an interaction length on the order of the atomic spacing. In the absence of long-ranged dispersion forces, and neglecting capillary fluctuations which lead to an additional repulsive contribution to Ψ(r) (see below), insertion of Eq. 2 into Eq. 1 leads to the prediction of a continuous premelting transition with an equilibrium grain boundary width that diverges logarithmically as T_M is approached from below. Recent theoretical results suggest that the nature of Ψ_{sr} can be much more complex. Diffuse-interface theories [8, 9] which neglect long-ranged forces and capillary fluctuations, have shown that the dependence of w on temperature may in some cases display a discontinuous jump, with the coexistence of “wet” and “dry” interface states, while other parameter choices lead to continuous increases in w up to T_M. In recent applications of the phase-field crystal (PFC) method to the study of grain boundary premelting [10, 11], results for 2D hexagonal systems give a disjoining potential that is purely repulsive above a critical misorientation [10], but exhibits a minimum, corresponding to a finite layer width at the melting point, below it.
While these theoretical models thus suggest a rich behavior for the disjoining potential in general, it remains unclear for which GB misorientations the various qualitative forms for $\Psi_{sr}(w)$ may be expected in real materials, and how structural short-range forces compare qualitatively to long range forces. To facilitate further progress in the understanding of the forces that drive premelting, we describe in the remainder of this Letter a quantitative framework for the direct calculation of $\Psi_{sr}(w)$, through histogram analyses of interface widths derived from MD.

Classical MD simulations provide a framework ideally suited for probing the short-ranged structural contributions to $\Psi(w)$. Such simulations have been employed extensively in the past to study GB premelting [13, 14] and in the present work we propose a methodology to extend the analysis of such MD results as a framework for extracting $\Psi(w)$. We demonstrate the approach for a classical model of elemental Ni, described by the embedded-atom potential of Foiles, Baskes and Daw [16]. The potential was chosen as we have previously calculated the solid-liquid interfacial free energies, melting temperature and solid-liquid thermodynamic properties with high precision. A value for $\gamma_{SL}$ of 285 mJ/m$^2$ for the potential has been determined using the capillary fluctuation method [15], and a coexistence technique was used to compute a melting temperature of 1710 $\pm$ 5K [17] (from subsequent coexistence runs and an analysis of GB width fluctuation data presented below the uncertainty in this estimate has been reduced to approximately 1 degree). We began by considering a total of four boundaries with a range of zero-temperature grain-boundary energies spanning 450 to 11431 mJ/m$^2$, which is 0.9 to 2.5 times the value of $\gamma_{SL}$. For each GB we performed a conjugate gradient minimization (exploring also the microscopic translational degrees of freedom and the excess number of atoms at the grain boundary) to derive an optimized zero-temperature interface structure. With this structure as a starting point the GBs were heated gradually up to the melting point employing constant-temperature MD simulations, particularly at the temperatures closest to $T_M$. After 4.2 ns equilibration runs at each temperature, statistics were obtained for $w$ at a given temperature as follows. For each snapshot (selected at a frequency of 10 ps) $w$ is determined by utilizing the scheme developed in the capillary fluctuation method [15]. Each atom is assigned a structural order parameter, $\phi_i$, constructed from the positions of the 12 nearest neighbor atoms and the $\phi_i$ values are then averaged in bins along the direction normal to the boundary. The point of inflection in the average order parameter profile is taken as the position of one of the solid-liquid interfaces. As described in more detail in the accompanying on-line material, the procedure is repeated to locate the second solid-liquid interface and hence the GB width.

An important observation in the present work is that the width of the GB regions is highly dynamic in the MD simulations, particularly at the temperatures closest to $T_M$. This point is illustrated clearly in Fig. 2 which shows three snapshots, taken from a 40 ns simulation at an undercooling of 2 K, where the atoms have been color coded based on their $\phi_i$ values; blue representing a liquid-like environment and red the crystal. The snapshots clearly demonstrate the presence of large fluctuations in the width of the premelted layer over the course of the simulation. The highly dynamic nature of the premelted layer provides a framework for extracting the disjoining potential. We show in Fig. 3 histograms of interface width obtained at five temperatures near the melting behavior, namely the $\Sigma 9$ boundary characterized by a 120° rotation about the GB normal lying along the [511] crystallographic direction. We study the structural properties of the grain boundary at five temperatures over a range of undercoolings 30 to 2 K below $T_M$. After 4.2 ns equilibration runs at each temperature, statistics were obtained for $w$ at a given temperature as follows. For each snapshot (selected at a frequency of 10 ps) $w$ is determined by utilizing the scheme developed in the capillary fluctuation method [15]. Each atom is assigned a structural order parameter, $\phi_i$, constructed from the positions of the 12 nearest neighbor atoms and the $\phi_i$ values are then averaged in bins along the direction normal to the boundary. The point of inflection in the average order parameter profile is taken as the position of one of the solid-liquid interfaces. As described in more detail in the accompanying on-line material, the procedure is repeated to locate the second solid-liquid interface and hence the GB width.

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point. The solid lines represent least-squares fits to the data employing the thermodynamic model of Eq. 1 as follows. The probability \( P(w) \) of observing a premelted layer width \( w \) is given as:

\[
P(w) = C \exp\left[-AG(w)/k_BT\right]
\]

(3)

where \( C \) is a temperature-dependent normalization constant, \( A \) is the cross-sectional area and \( G(w) \) is defined in Eq. 1. The data in Fig. 3 suggests a logarithmic divergence of \( w \) with increasing temperature, and in order to fit Eq. 3 to the MD data, we therefore employ the form for the disjoining potential given in Eq. 2. The least square fit Eq. 3 to the MD data, we therefore employ the form for the disjoining potential in Eq. 1. The data in Fig. 1 suggests a logarithmic divergence of \( w \) with increasing temperature, and in order to fit Eq. 3 to the MD data, we therefore employ the form for the disjoining potential in Eq. 2. The least square fit Eq. 3 to the MD data, we therefore employ the form for the disjoining potential in Eq. 1. The data in Fig. 1 suggests a logarithmic divergence of \( w \) with increasing temperature, and in order to fit Eq. 3 to the MD data, we therefore employ the form for the disjoining potential in Eq. 2.

FIG. 2: Snapshots from an MD simulation at an undercooling of 2 K illustrating the dynamic nature of the GB width. The red (blue) areas indicate regions of solid (liquid) like liquid order. The liquid-like regions at the far left and right hand sides represent premelting of the free surfaces of the simulation cell, while that in the middle corresponds to the premelted grain boundary.

The present simulations have quantified only the short-ranged contribution to \( \Psi(w) \). However, for setting the temperature scale over which premelting can be observed in elemental metals, we estimate that this is the dominant contribution. For values of \( w \sim 1 \text{ nm} \) we can estimate an upper bound on the dispersion forces using a value of the Hamaker constant measured for surface premelting of metals [12]. This gives a contribution to \( \Psi(w=1 \text{ nm}) \sim 4 \text{ mJ/m}^2 \), approximately one order of magnitude smaller than the results presented in Fig. 4, computed from the value of \( \Psi_{sr} \) using the parameters derived above. There is also a known entropic contribution to \( \Psi(w) \) associated with the long-wavelength fluctuations of the two interfaces for large separation [19]. This contribution is generally repulsive because the conditions that the two interfaces do not intersect reduces the available configurational entropy of interface meandering. While this entropy reduction produces a physically important long-range force for one-dimensional interfaces, such as step

The analysis of Fig. 3 assumed a melting point of \( T_M = 1710 \text{ K} \). If instead a value of just one degree different, i.e., \( T_M = 1709 \), is assumed, then a poor fit to \( P(w) \) is obtained at the lowest undercooling. In addition, for simulations run at a temperature of \( 1712 \text{ K} \) the system exhibited a gradual melting. These findings, together with the results of separate coexistence simulations, indicate that the melting temperature is known to a precision approaching ±1º.

As an independent check on the validity of Eq. 2 we employ an additional analysis of the data of Fig. 3. From Eq. 3 the disjoining potential can be written in terms of \( P(w) \) as:

\[
\Psi(w) = -(k_BT/A)lnP(w,T_i) - \Delta G_f w + a_i
\]

(4)

where the \( a_i \) are unknown constants related to \( C \) in Eq. 1 and the subscript \( i \) denotes a separate histogram of data corresponding to each undercooling. The \( a_i \) can be determined by a least square fitting procedure such that all the data sets can be merged and the entire function \( \Psi(w) \) constructed. Notice the procedure adopted here is analogous to the histogram method, often employed in Monte Carlo simulations to extract transition states and energy barriers, but with the undercooling playing the role of a bias potential. The results of the histogram procedure are shown in Fig. 3. The inset of the figure plots the right-hand side of Eq. 3 with all the constant terms set to zero to illustrate that different undercoolings sample a range of \( w \) regimes of \( \Psi(w) \). The main figure shows the final \( \Psi(w) \) function along with a fit (solid line) to the exponential form given in Eq. 2. It is important to note that the fit parameters obtained via the histogram method (\( \delta = 2.49 \text{kA} \) and \( \Delta \gamma = 156 \text{mJ/m}^2 \)) compare very well to those derived through the individual fits of the separate histograms in Fig. 3. \( \delta = 2.67 \pm 0.18 \text{kA} \) and \( \Delta \gamma = 127 \pm 26 \text{mJ/m}^2 \).

FIG. 3: The distribution function \( P(w) \) vs \( w \) from the MD simulations (symbols) versus the least square fits of the premelting model of Eqs. 1 and 2.
ledges on surfaces, it produces only a subdominant short-range forces for two-dimensional interfaces owing to the slow logarithmic growth of the mean-square fluctuation amplitude with interface area, as compared to the much faster square-root growth of this amplitude with interface length in one dimension. In particular, a straightforward estimate of this force using analytical results of the literature [18] and the parameters for Ni from the MD results show that this entropic force is completely negligible in comparison to the short-range structural forces computed here.

Thus, for high-energy boundaries it can be expected that the lowest temperatures where premelting will become appreciable is set through the relation \( \Delta T/T_M = (\Delta \gamma/L \rho \delta) \exp(-w_{eq}/\delta) \), with \( w_{eq} \sim 1 \text{ nm} \), where we have expressed \( \Delta G_f = L \Delta T \rho / T_M \) in terms of the latent heat per atom \( (L) \), the solid density \( (\rho) \) and the undercooling \( (\Delta T = T_M - T) \). The present results give \( \delta \) on the order of an interatomic spacing and \( \Delta \gamma \) on the order of half \( \gamma_{SL} \). While the exact values will vary somewhat depending on the system, we believe these values are well representative of high-energy boundaries in pure metals. With these estimates we obtain a value of \( \Delta T \) required to obtain \( w \sim 1 \text{ nm} \) of \( (\Delta T/T_M) \sim (\alpha/2) \exp(-4) \), where we have used \( \rho \delta^{1/3} \sim 1 \) and the relation \( \gamma_{SL} \rho^{-2/3}/L = \alpha \), where \( \alpha \) is the Turnbull coefficient [19] which has a roughly constant value of about 0.5 for elemental metals [18]. The estimate of the undercooling required for a 1 nm premelted film is thus \( \Delta T/T_M \sim 0.005 \). The results are consistent with the experimental studies of Ballufi and co-workers [17] who estimated a lower bound of \( T = 0.999 T_M \) for the temperature where boundary widths of a few nm could be observed experimentally.

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