Melting at dislocations and grain boundaries: A Phase Field Crystal study

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Dislocation and grain boundary melting are studied in three dimensions using the Phase Field Crystal method. Isolated dislocations are found to melt radially outward from their core, as the localized excess elastic energy drives a power law divergence in the melt radius. Dislocations within low-to-mid angle grain boundaries melt similarly until an angle-dependent first order wetting transition occurs when neighboring melted regions coalesce. High angle boundaries are treated within a screening approximation, and issues related to ensembles, metastability, and grain size are discussed.

Freezing and melting transitions do not exhibit the range of universal behavior associated with continuous phase transitions and largely for this reason have eluded a unified theoretical description. The nature of a given melting transition may depend sensitively on the details of the system and experiment, and can involve many distinct processes both within and between multiple forms of excitations. For example, melting may occur abruptly and discontinuously at the melting temperature $T_m$, or it may initiate well below $T_m$ at surfaces and/or internal defects and proceed up to $T_m$. This process of premelting has been studied extensively for surfaces \cite{1,2} and is relatively well understood, but limited and inconsistent experimental evidence for melting at dislocations and grain boundaries leaves a number of issues unresolved.

A recent study of colloidal crystals has verified that premelting does occur at vacancies, dislocations, and grain boundaries, and has provided measurements of the localized premelting behavior below $T_m$. \cite{3}. The conditions which determine whether premelting will occur continuously or discontinuously, and whether the width of the premelted region diverges are not fully understood. Grain boundaries in Al have been found to liquify very near $T_m$ and the width of the melted layer appears to diverge \cite{4}. Discontinuous jumps in grain boundary diffusion coefficients \cite{5,6}, mobility \cite{7}, and shear resistance \cite{8} have been found in other metals.

Theoretical studies have been based on either explicitly atomistic methods such as Molecular Dynamics \cite{9,10} and Monte Carlo \cite{11}, or on continuum phase field models with uniform phases \cite{12,13,14}. In this study, dislocation and grain boundary melting are examined using the Phase Field Crystal (PFC) method \cite{15}, which extends the phase field approach to the level of atomistic resolution. This permits straightforward identification of stable equilibrium and metastable nonequilibrium atomic structures, while inherently including crystal symmetry and orientation, elasticity/plasticity, and the individual dislocations which compose the grain boundaries. Our description will be most applicable to hard-sphere/colloidal systems and possibly simple metals.

The melting behavior of dislocation pairs and symmetric tilt grain boundaries of $\theta = 4^\circ$, $8^\circ$, $16^\circ$, $24^\circ$, $32^\circ$, and $44^\circ$ are examined numerically for a simple PFC model with bcc symmetry. Analytic results are derived for isolated dislocations and low $\theta$ boundaries by combining the PFC equations with continuum linear elasticity. A screening approximation is outlined for high angle boundaries, though somewhat surprisingly, the low $\theta$ description is found to remain reasonably accurate for high $\theta$.

As shown in reference \cite{16} the PFC free energy can be derived from the Ramakrishnan-Yussouff free energy functional of classical density functional theory \cite{17,18}. Here we give the final form:

$$F = \int d\vec{r}\left[\frac{B^s}{2}n^2 + \frac{B^o}{2}\n(2\nabla^2 + \nabla^4)n - v\frac{n^3}{6} + \frac{n^4}{12}\right]$$

where $F \equiv \langle F - F_o \rangle / (\rho k_B T L^d)$, $F_o$ is the free energy functional at constant density, $\bar{\rho}$ is the average number density, $k_B$ is Boltzmann’s constant, $T$ is temperature, $L \equiv \sqrt{2|C_4|/C_2}$, $C_i$ is the $i$ point direct correlation function of the reference liquid state, $B^o \equiv 1 - \bar{\rho} C_0$, $B^s \equiv \bar{\rho} (C_2)^2 / 4|C_4|$, $\vec{r} = \vec{x}/L$ and $v$ accounts for the lowest order contribution from $C_3$, $n = (\rho - \rho_L)/\rho_L$ is the scaled number density, where $\rho$ is the local density variable and $\rho_L = \bar{\rho}$ is the liquid number density. Classical density functional theory has been used to examine surface melting \cite{2,19}, but not grain boundary melting, presumably due to the complexity of the solid-solid interface and the more demanding system size requirements.

The dynamics are given in dimensionless form by

$$\frac{\partial n}{\partial \tau} = \nabla^2 \delta F / \delta n + \eta$$

where $\langle \eta(\vec{r}_1, \tau_1)\eta(\vec{r}_2, \tau_2) \rangle = M\nabla^2 \delta(\vec{r}_1 - \vec{r}_2)\delta(\tau_1 - \tau_2)$ and $M \equiv 3(\bar{\rho} L^d)^2$. This form imposes a constant density and is consistent with the canonical ensemble.

A semi-implicit pseudospectral algorithm was used to solve Eq. \cite{2} in three dimensions with periodic boundary
conditions. The parameters used were $\Delta x = 0.976031$, $\Delta \tau = 0.5$, $B^* = \sqrt{3}/3$, $v = 3^{1/4}/2$, and $M = 0.002$. A system size $V = (512\Delta x)^3 = (56a)^3$ was used for the dislocation pair and $4^\circ$ grain boundary pair, while $V = (256\Delta x)^3 = (28a)^3$ was used for all other grain boundary pairs, where $a = 8.9237$ is the bcc lattice constant. Finite size effects increase as $\theta$ decreases, but were found to be small for all grain boundaries studied. The gaussian width or mean square displacement ($D$) of each localized density peak was monitored as the temperature $\Delta B \equiv B' - B^*$ was increased toward the melting point. The local crystallinity $\phi$ has been defined as $\phi(\vec{r}) = (D(\vec{r}) - D_X)/(D_L - D_X)$, where $D_X$ is the equilibrium $D$ of the crystal phase and $D_L$ is that of the liquid phase. $\phi = 1/2$ specifies a liquid-solid interface.

The radius of melted region around a dislocation core $R_m$ was first measured in this manner for an edge dislocation pair as the temperature was raised toward the bulk melting temperature $\Delta B_m$. The results are shown in Fig. 1 where the data is plotted as $(R_m + R_0)^{-2}$ vs $\Delta B$ to demonstrate that $R_m$ is consistent with a $(\Delta B_m - \Delta B)^{-1/2}$ form which will be derived later. $R_0$ is an offset related to the finite size of the dislocation core at zero temperature. The fit to this form predicts a bulk melting temperature $\Delta B_m = 0.0270$ which is in good agreement with the directly measured value of $\Delta B_m = 0.0278$. The upper inset of Fig. 1 shows melting around an edge dislocation as $\Delta B \rightarrow \Delta B_m$.

Figure 2 shows the progression of melting at $8^\circ$ and $44^\circ$ grain boundaries. Low angle boundaries were found to first melt radially at each dislocation core, until the melted regions of neighboring dislocations coalesce and a uniform wetting layer is formed along the boundary. Individual dislocations cannot be distinguished in high angle boundaries, and melting in this case was found to proceed by uniform disordering along the boundary rather than by local radial melting. Interfacial roughening due to thermal fluctuations is negligible in all simulations presented here.

The dependence of the width of the wetting layer (or the liquid volume fraction of the system) on $\Delta B$ is shown in the inset of Fig. 3 for various grain boundary angles. In all cases the width remains narrow and the boundary relatively dry until above the solidus, at which point a discontinuous jump is observed at some characteristic wetting temperature $\Delta B_{\text{wet}}$. The dependence of $\Delta B_{\text{wet}}$ on $\theta$ is shown in the main plot of Fig. 3. The fit lines will be discussed in the following, though the axes of the plot reveal already that our predicted form will be $\Delta B_{\text{wet}} \propto \sin^2 \theta$.

Based on these simulation results, we have developed a theory of dislocation-driven melting, which is easily extended to low angle grain boundaries. The low angle results are shown to remain accurate for all but the high-
est \( \theta \) where the dislocation spacing \( d \) reaches the order of the burger’s vector \( b \). A screening approximation for the spatial grain boundary energy is found to be more applicable for very large \( \theta \), with a gradual crossover taking place between these two regimes.

According to continuum elasticity \cite{20}, the radially averaged elastic energy density per length of dislocation line in a three-dimensional isotropic solid is \( F_{el} = \alpha \mu / R^2 \), where \( \mu \) is the shear modulus. For a screw dislocation \( \alpha_s = b^2/4\pi^2 \) and for an edge dislocation \( \alpha_e = \alpha_s/(1-\sigma) \) where \( \sigma \) is the Poisson ratio. If we assume this result to hold for a dislocation in the PFC model, at distances approaching the core region, then \( R_m \) can be directly calculated by determining the distance at which \( F_{el} \) is sufficiently large to destabilize the crystalline phase, melting the dislocation core.

It will be assumed that \( n \) can be represented in a one mode approximation for a bcc lattice, i.e., \( n(r^2) = A (\cos qx \cos qy + \cos qz \cos qz + \cos qy \cos qz) \). Substituting \( n \) into Eq. (1) and minimizing with respect to \( q \),

\[
\Delta f^X = \frac{3}{8} \Delta B A^2 - \frac{v}{8} A^3 + \frac{45}{256} A^4 \tag{3}
\]

where \( \Delta f^X \equiv (F - F_L)/V \), \( F_L \) is the free energy of the liquid, \( V = (2\pi/\alpha)^3 \), and \( q_{min} = \sqrt{2}/2 \). The shear modulus can be estimated in the one mode approximation by setting \( n(x, y, z) \rightarrow n(x + \zeta y, y, z) \) and expanding \( F \) in \( \zeta \) such that \( F = F(\zeta = 0) + \mu \zeta^2 + \cdots \). This procedure gives \( \mu/k_B T L^2 \rho = A^2 B^*/8 \). The total (dimensionless) free energy of the system with a dislocation is then \( \Delta f^X + F_{el}/k_B T \rho L^2 \), which can be written

\[
\Delta f = \frac{3}{8} \left( \Delta B + \frac{E}{R^2} \right) A^2 - \frac{v}{8} A^3 + \frac{45}{256} A^4. \tag{4}
\]

where \( \tilde{R} \equiv R/b \) and \( E_s \equiv B^*/(12\pi^2) \), \( E_c \equiv E_s/(1-\sigma) \) for screw and edge dislocations respectively. Equation (4) indicates that the elastic energy ‘shifts’ the effective temperature \( \Delta B \) by an amount \( E/R^2 \). The implication is that the liquid-solid transition is shifted and instead of occurring when \( \Delta B = \Delta B_m \) occurs when \( \Delta B + E/R^2 = \Delta B_m \). Thus the premelt radius can be written

\[
\tilde{R}_m = \sqrt{E/(\Delta B_m - \Delta B)} \tag{5}
\]

or \( 1/\tilde{R}_m^2 = (\Delta B_m - \Delta B)/E \).

As shown in Fig. 1, this form is consistent with the simulation results for edge dislocation pairs, though the predicted slope \((1/E_s) \) is in error by a factor of nearly five. A more definitive test would require additional data very near \( \Delta B_m \), a region increasingly difficult to access due to system size requirements.

Extending this result to low angle boundaries, we can estimate the grain boundary wetting temperature \( \Delta B_{wet} \) where neighboring dislocations coalesce by setting \( R_m = d/2 = 1/(2 \sin \theta) \). Substituting Eq. (1) for \( R_m \) gives

\[
\Delta B_{wet} = \Delta B_m - 4E \sin^2 \theta \tag{6}
\]

which is in good agreement with the data shown in Fig. 3.

This result should lose accuracy as \( \theta \) increases since the dislocation energies gradually deviate from the isolated dislocation result as \( \theta \rightarrow \theta_{max} \). The agreement up to \( \theta \approx 32^\circ \) is somewhat unexpected as the superposition generally loses accuracy for \( \theta \gtrsim 10^\circ \). The best fit line predicts \( \Delta B_m = 0.0272 \), again near the measured value.

The solid line in Fig. 3 corresponds to the fit line from Fig. 1 set equal to \( 1/(2 \sin \theta) \) and solved for \( \Delta B_{wet} \). The agreement here clearly indicates that the wetting of low and mid-angle grain boundaries is accurately described by the coalescence of radially melted regions around nearly isolated dislocations.

In the limit of large \( \theta \) (\( d \rightarrow 0 \)), the grain boundary energy becomes increasingly uniform along its length (see Fig. 2) and can no longer be described in terms of individual dislocations. We expect that elastic fields at long distances are screened by closely spaced dislocations, giving rise to exponentially decaying spatial grain boundary energy. Indeed, direct analysis of free energy data from simulations indicates that such an exponential form is qualitatively correct. Solving for \( \Delta B_{wet} \) using \( F_{el} \propto e^{-x/b} \) rather than \( F_{el} \propto 1/R^2 \) gives \( \Delta B_m - \Delta B_{wet} \propto e^{-f(\theta)} \). This is the form of the wide dashed line in Fig. 3 which appears to be more appropriate for large \( \theta \).

Some comments concerning the influence of liquid-solid coexistence and the canonical ensemble (i.e., conserved density) on grain boundary melting may be helpful at this point. The equilibrium state for a simple system with a grain boundary is most generally either dry if \( F_{gb} < 2F_{ls} + \ell(F_L - F_X) \) or wet if \( F_{gb} > 2F_{ls} + \ell(F_L - F_X) \), where \( F_{gb} \) is the grain boundary energy, \( F_{ls} \) is the energy

![FIG. 3: Grain boundary wetting temperature vs. \( \sin^2 \theta \). Fit lines are discussed in the text. Inset: Liquid volume fraction vs. \( \Delta B \) for a various grain boundaries. The dotted line corresponds to the liquid volume fraction predicted for the 8° boundary based on Eq. (5) only (ignoring coexistence).](image)
of a liquid-solid interface, and $\ell$ is the width of the li-
quid region in the wet state. If the wet state becomes
favorable below the melting temperature, then a grain
boundary wetting transition occurs. In the canonical en-
semble as examined here, the effects of liquid-solid coex-
istence and the subsequent shifts in density of the two
phases above the solidus $\Delta B_{sol}$ modify this heuris-
tic argument. Now $\Delta B_m$, the temperature at which $F_L = F_X$, is straddled by a coexistence region. As $\Delta B \rightarrow \Delta B_m$ the
system first encounters a solidus above which some vol-
ume fraction of liquid will minimize the overall $F$.

For the grain boundary pair geometry, the equilibrium state
above $\Delta B_{sol}$ is one with a uniform volume of liquid occu-
pying each boundary region. Therefore, an equilibrium
first order wetting transition will occur at $\Delta B_{sol}$ as long
as the grain size is not excessively small. Above $\Delta B_{sol}$,
the liquid layer width will be controlled by coexistence
rather than local defect energies, since the elastic fields
of the grains largely decouple ($F_{gb} \rightarrow 0$) upon wetting.

The results presented here show no wetting or strong
premelting for $\Delta B \leq \Delta B_{sol}$, and the equilibrium wet-
ting transition is not observed. Instead, a $\theta$-dependent
discontinuous transition from the metastable dry bound-
ary state to the equilibrium wet state occurs at $\Delta B_{sol} < \Delta B_{wet} < \Delta B_m$, as shown in the inset of Fig. 3. This is
because the wetted state is not nucleated in observable
times until $R_m$ has grown sufficiently large to coalesce
and the free energy barrier approaches zero. The disloca-
tions and/or grain boundaries act as nucleation sites for
the liquid above $\Delta B_{sol}$, creating well-defined nonequi-
librium paths from the metastable dry state to the $F$
minimizing wet state (which all must conserve $\rho$).

The condition for wetting in the canonical ensemble
involves the grain size $L_g$, such that wetting can be
suppressed to temperatures above $\Delta B_{sol}$ when $L_g$
is finite. The condition can be written $F_{gb} + L_g \Delta F_X > 2 F_L + \ell \Delta F_C$ where $\Delta F_X = F_X[\rho] - F_X[\rho X]$ and $\Delta F_C = F_L[\rho L] - F_X[\rho X]$. Here $\ell = (\rho X - \bar{\rho})/(\rho X - \rho L)$, $\bar{\rho}$ is the
conserved system density, and $\rho X$ and $\rho L$ are the shifted
coeexistence densities of the solid and liquid phases, re-
spectively. For $\Delta B \leq \Delta B_{sol}$, if we assume that $\Delta F_X = 0$
and $\rho L = \rho X = \bar{\rho}$ (this is not the case when premelting
is strong below $\Delta B_{sol}$), we recover the original inequality
$F_{gb} > 2 F_L + \ell (F_L - F_X)$ and $L_g$ is not a significant factor.
In the limit $L_g \rightarrow \infty$, the wetting condition will always
be satisfied for $\Delta B > \Delta B_{sol}$ and the equilibrium
transition occurs at $\Delta B_{sol}$. As $L_g$ decreases, the equilibrium
wetting transition is shifted to higher $\Delta B$.

Two-dimensional systems show qualitatively similar
results to those presented above. Preliminary simula-
tions have also been conducted in the grand canonical
ensemble (i.e., non-conserved density), where the above
complications with liquid-solid coexistence due to den-
sity conservation can be avoided. Initial results indicate
that there is no strong wetting transition in this case, as
the atoms near grain boundaries continuously delocalize
toward $\Delta B_m$ but do not liquify and decouple the grains
until above $\Delta B_m$.

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