CMSN Newsletter

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In this issue:

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Research Highlight

In this issue of the *CMSN Newsletter*, we feature a research highlight from the Dynamics and Cohesion CRT: "Interfacial Premelting in Hot Materials: Recent Insights from Integrated Atomistic and Mesoscale Simulations."

Interfacial Premelting in Hot Materials

Recent Insights from Integrated Atomistic and Mesoscale Simulations

DYNAMICS AND COHESION OF MATERIALS INTERFACES AND CONFINED PHASES UNDER STRESS CRT

***Summary*:** The mechanical behavior of structural materials at high homologous temperatures can be dramatically altered by the formation of nanometer-scale films with liquid-like properties, spatially confined at the boundary between misoriented grains. To understand basic interfacial phase-transition aspects of this phenomenon in metals and alloys, the DCMICPUS cooperative research team (CRT) has integrated novel atomistic and mesoscale computational methods for quantitative studies of grain-boundary premelting. This effort has led to fundamental new insights into the nature of the "disjoining forces" that energetically favor the formation of premelted films below the bulk melting point (T_M) by effectively pushing apart crystal-liquid interfaces between misoriented grains. Insights were made possible by the development of new methods for the direct calculation of these forces in pure systems and the first quantitative simulation study for an alloy. These developments represent important advances in the modeling of polycrystalline structural materials under extreme conditions of temperature and stress.

Premelting at solid surfaces is well established, having been observed in a wide variety of crystalline materials ranging from metals to molecular solids [1]. The phenomenon has important consequences for a variety of natural processes; for example, the surface premelting of ice is responsible for frost heaving, electrical charge accumulation in thunderclouds, and even ice skating. Premelting at internal interfaces, in particular grain boundaries (see Figs. 1 and 2), can have similarly dramatic consequences in the context of materials processing and the physical properties of polycrystals at high homologous temperatures. In some cases, grain-boundary premelting can lead to catastrophic failure, e.g., due to accelerated creep; on the other hand, the formation of amorphous intergranular films in ceramics is an example where premelting can enhance the toughness of a material. Despite the importance of this phenomenon, direct experimental observations remain relatively rare, particularly for pure materials [2]. As a consequence, a number of outstanding fundamental questions remain concerning the nature of the forces that drive grain-boundary premelting and their dependence on interface structure and composition.

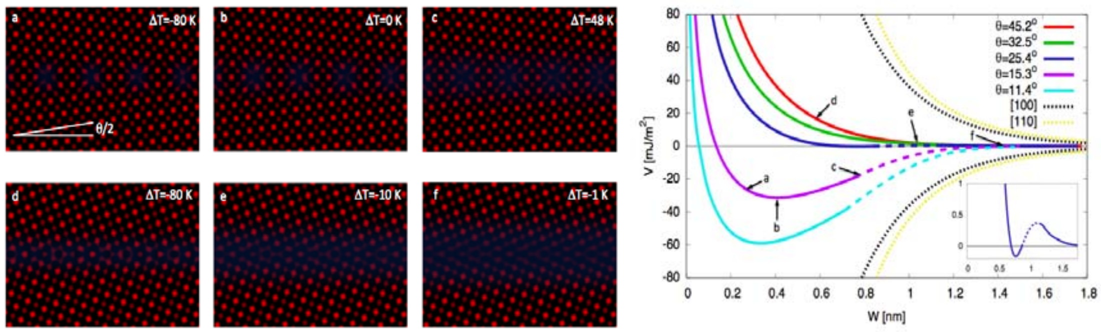

Fig. 1: The left-hand figures represent reconstructed atomic densities at [100] symmetric tilt boundaries in bcc Fe, studied by a continuum Ginzburg-Landau approach derived from the phase-field crystal model. Dark regions represent areas of liquid-like disorder. Calculated disjoining potentials are shown on the right and demonstrate a transition from attractive to repulsive behavior with increasing misorientation. Disjoining forces correspond to the derivative of these potentials with respect to the film thickness w. Also shown for comparison are longer-range potentials (dotted black and yellow lines) for two crystals of the same orientation that become strongly repulsive when one crystal is shifted by half a lattice spacing relative to the other in a plane normal to [100] (black) or [110] (yellow).

Grain-boundary premelting in a pure system can be understood to reflect a competition between two opposing thermodynamic factors: the bulk free-energy difference between solid and liquid, which at temperatures below T_M penalizes the formation of the liquid layers, and a thickness (w) dependent interfacial free energy (γ). Under wetting conditions, the latter favors replacing a dry solid-solid interface (with interfacial free energy γ_{gb}) by two solid-liquid interfaces (with energy $2\gamma_{sl}$). The form of $\gamma(w)$ itself is known to be governed by competing long- and short-ranged contributions. The former, which are associated with van der Waals dispersion forces, are known to be attractive in nature (favoring finite w) and are relatively well characterized [3]. The short-ranged contributions, which are dominant for nanometer-scale values of w, remain far less understood. These contributions are typically assumed to be describable by a simple exponential dependence of γ on w. However, recent work by members of this CRT [4] has extended earlier phase-field-model calculations [5-6], demonstrating a much richer variety of behavior associated with both first-order and continuous premelting transitions.

To provide more quantitative insights, new continuum methods for studying grain-boundary premelting have been developed within the framework of the phase-field crystal (PFC) method [7-8] and Ginzburg-Landau theory [9]. Those methods make it possible to accurately compute the excess interfacial free energy resulting from the overlap of crystal density fields of two misoriented grains [8]. Examples from this approach are shown in Fig. 1 for a new Ginzburg-Landau model parameterized by atomistic simulations for bcc Fe [9, 10]. This model uses complex order parameters to represent crystal density waves with spatially varying amplitudes and directions within the disordered grain-boundary region. Results are shown for low-angle (low-energy) and high-angle (high-energy) grain boundaries and demonstrate both "attractive" and "repulsive" behavior, respectively, for these two cases. In the former case, grain boundaries must be superheated above T_M before a complete liquid layer forms along the length of the boundary; below T_M extensive disorder is present only within the core regions of boundary dislocations. At higher misorientations continuous liquid films are observed to form at temperatures well below T_M. Calculated values for the *disjoining potential*, defined as $V(w)=\gamma(w)-2\gamma_{sl}$, are shown on the right-hand side of Fig. 1 as a function of misorientation. A transition from purely repulsive behavior at large misorientations (θ), to a non-monotonic behavior featuring a minimum at small w for low misorientations, is apparent. For large values of θ, the calculated disjoining potentials are consistent with a continuous premelting transition, associated with smoothly increasing values of w as the temperature is increased. At intermediate misorientations an interesting prediction, illustrated in the inset of the right panel in Fig. 1, is that the disjoining potential possesses a repulsive barrier, giving rise to first-order behavior.

In order to further the development of coarse-grained theories for interfacial premelting, it is important to establish a simulation-based tool to accurately probe the thermodynamic forces associated with structural interactions across a disordered grain boundary. Such an approach was recently developed by members of this CRT, based on an analysis of equilibrium fluctuations in the width of premelted layers at high temperatures [11]. This approach is illustrated in Fig. 2, showing results obtained for a high-energy boundary in elemental Ni. In the images on the left-hand side, atoms are colored based on the values of a local structural order parameter – red corresponding to highly ordered crystalline-like environments, and blue to disordered, liquid-like environments. An important observation is that the width of the premelted layers is highly dynamic, as illustrated by the three snapshots taken from different times in a relatively long molecular-dynamics simulation. From an analysis of the associated equilibrium width histograms, at several different temperatures below T_M, the disjoining potential can be directly constructed, as illustrated in the plot on the right-hand side of Fig. 2. From an analysis of the magnitudes of the calculated disjoining potentials, and the known scaling of γ_{sl} with density and the latent heat of melting, it is concluded that, quite generally, grain-boundary premelting in pure materials should be observable only within very narrow temperature ranges near T_M [11], consistent with the previous experimental studies [12].

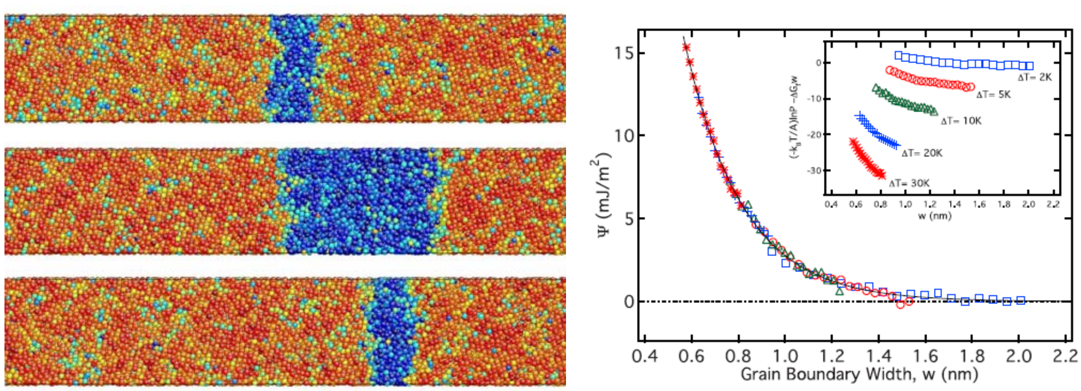

Fig. 2: Atomistic simulation snapshots for a premelted grain boundary in Ni are shown on the left. An analysis of the equilibrium fluctuations in the width of the premelted layer allow extraction of the disjoining potential ($\psi(w)=\gamma(w)-2\gamma_{sl}$) shown on the right (from [11]).

The results summarized above represent significant advances in the quantitative characterization of the forces underlying grain-boundary premelting phenomena in pure metals. This work has been motivated by an overall goal of the DCMICPUS project to develop multiscale frameworks for modeling the microstructural stability and mechanical behavior of polycrystalline materials relevant for energy-related applications under the extreme conditions of high temperature and stress. To address such applications requires generalization of the methods described above, beyond pure materials. An important recent step in this direction is the first detailed simulation study of grain-boundary premelting behavior in a binary alloy system by members of this CRT [13]. This work has demonstrated the formation of thin layers of the liquid phase when the grain composition approaches the solidus in a model binary eutectic system. The liquid layer thickness was found to remain finite and the boundary can be overheated/oversaturated to metastable states slightly above the solidus. The combination of such simulations with the analysis techniques described above open new possibilities for investigating compositional effects on premelting behavior and for understanding grain-boundary cohesion in alloys at high temperatures.

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Conferences and Workshops

Two CMSN CRTs will be holding coordination meetings. These include the following:

- *Resonant Inelastic X-Ray Scattering* Coordination Meeting (satellite meeting to the APS March Meeting), Pittsburg, PA, March 15, 2009
- *Multiscale Simulation of Thermo-Mechanical Properties in Irradiated Fission-Reactor Materials* Coordination Meeting, University of Florida, Gainesville, FL, March 11 & 12, 2009

CMSN APS March Meeting Talks

Predictive Capability for Strongly Correlated Systems CRT:

- Dynamic Cluster Monte Carlo Study of the Single-Particle Spectra of Strongly-Interacting Fermion Gases - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-002563.pdf
- Electronic Coupling and Optimal Gap Size within a Metal Nanoparticle Dimer Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-003254.pdf
- Realistic simulation of Kondo lattice model: application to Cerium compounds – Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-003971.pdf
- Structural, spin, and orbital phase transitions in LaOFeAs: I. Total energy calculations – Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-007415.pdf
- Structural, spin, and orbital phase transitions in LaOFeAs: II. Wannier function analysis – Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-007420.pdf
- Unusual electronic states in TiO_2/VO_2 (001) multilayers Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-003669.pdf
- Mott-like behavior in the pseudogap region of the Hubbard model – Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-005848.pdf
- Self-consistent solution for the Hubbard model at the two-particle and one-particle level using the parquet formalism – Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-001970.pdf
- Spatially inhomogeneous phase in the two-dimensional repulsive Hubbard model – Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-003111.pdf
- Inhomogeneous ground state in the Hubbard model: a mean-field study Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-006334.pdf
- Ground-state properties of simple solids from GW calculations – Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-001765.pdf
- High Precision QMC Study of the 2D Hubbard Model – Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-006285.pdf

- Multideterminant quantum Monte Carlo calculations of benzene dimers Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-007664.pdf
- Auxiliary-Field Quantum Monte Carlo Studies of Pressure-Induced Phase Transitions in Silicon and MnO – Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-003022.pdf
- LDA+DMFT Charge Self-consistency Applied to Yb Valence Transition Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-003829.pdf

Resonant Inelastic X-Ray Scattering CRT:

- ARPES matrix element and the waterfall effect in the cuprates Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-005131.pdf
- Mott gap collapse in the cuprates -- apparent or real? Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-002729.pdf
- Momentum density, Fermi surface and directional Compton profile in the Iron-based superconductor LaOFeAs - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-001763.pdf
- Convergence of the variational parameter without convergence of the energy in Quantum Monte Carlo (QMC) calculations using the Stochastic Gradient Approximation - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-001560.pdf
- Circular dichroism in angle-resolved photoemission spectrum as a technique to probe symmetry breaking in $Bi_2$$Sr_2CaCu_2O_{8+\delta}$ - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008- 002148.pdf
- Role of Oxygen Electrons in the Metal-Insulator Transition in the Mangnetoresistive Oxide $La_{2-2x}Sr_{1+2x}Mn_2O_7$ - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-001878.pdf
- Origin of electron-hole asymmetry in the scanning tunneling spectrum of $Bi_2Sr_2CaCu_2O_{8+\delta}$ - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-001612.pdf
- Charge-ordering in Magnetite Studied by Magnetic Compton Scattering Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-002674.pdf
- Strong correlation effects and optical conductivity in electron doped cuprates Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-001416.pdf
- Quasiparticles in Bi-2212 – Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-005644.pdf
- ARPES study on Tl-based Cuprates – Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-002502.pdf
- High-energy anomaly in hole- and electron-doped cuprates – Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-003580.pdf
- Evaluation of time-resolved photoemission spectra from nonequilibrium, time-domain Green functions - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-003542.pdf

- Quasi-zero dimensional CuB_2O_4 as an archetype for resonant inelastic X-ray scattering - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-001483.pdf
- Momentum-Resolved Cu K-edge RIXS Spectra in the Insulating Parent Compounds of High Tc Superconductors - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-005753.pdf
- The Impact of an Oxygen Dopant in an ideal $Bi_2Sr_2CaCu_2O_{8+\delta}$ Crystal - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-002968.pdf
- Quasiparticle scattering from impurities in the cuprates - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-003550.pdf
- Many-Pole Self-Energy Model Corrections to Kohn-Sham Calculations of Excited State Spectra - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-006094.pdf
- RT-TDDFT simulation of the optical properties of a model organic photovoltaic device - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-001817.pdf
- High-performance computational condensed-matter physics in the cloud - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-001854.pdf
- *Ab initio* Bethe-Salpeter Equation approach for aperiodic materials and core-excitations - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-003466.pdf
- Spin-orbital frustrations and anomalous metallic state in iron-pnictide superconductors - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-002417.pdf
- Multiferroicity in half-doped manganites - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-004461.pdf
- Probing orbitons in YTiO3 with Resonant Inelastic X-ray Scattering - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-004786.pdf
- Resonant soft x-ray scattering from Cu valence modulations in oxygen ordered YBCO - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-000772.pdf
- Numerical study of relaxation dynamics in photoexcited states of one-dimensional Mott insulators - Preview Abstract: http://absimage.aps.org/image/MWS_MAR09-2008-003486.pdf

Please consult the CMSN website for updated information on conferences and workshops, at http://www.phys.washington.edu/~cmsn/.

CMSN Information

CMSN's teams, oversight, and administration are listed below. Further information can be found at http://www.phys.washington.edu/~cmsn.

Cooperative Research Teams	Leaders
Dynamics and Cohesion of Materials Interfaces and Confined Phases Under Stress	Mark Asta (University of California at Davis), Alain Karma (Northeastern), and Anthony Rollett (Carnegie-Mellon)
Predictive Capability for Strongly Correlated Systems	Richard Scalettar and Warren Pickett (UC-Davis)
Multiscale Simulation of Thermo-mechanical Processes in Irradiated Fission-reactor Materials	Dieter Wolf (INL) and Simon Phillpot (University of Florida)
Resonant Inelastic X-Ray Scattering	Arun Bansil (Northeastern University), Jim Freericks (Georgetown University), Bob Markiewicz (Northeastern University), Michel van Veenendaal (Northern Illinois University and Argonne National Laboratory)
Predictive Modeling of the Growth and Properties of Energy-Relevant Thin Films and Nanostructures	Kai-Ming Ho (University of Iowa and Ames Laboratory) and Zhenyu Zhang (University of Tennessee and Oak Ridge National Laboratory)

CMSN Oversight

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