Correlation and Dynamics in Metallic Liquids

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OUTPUT SUMMARY – FY2003-2005

Invited Conference Presentations	20
Other Invited Presentations	14
Contributed Presentations	9
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ABSTRACT AND BACKGROUND

In order to advance our fundamental understanding of the driving forces and associated response mechanisms that ultimately govern local and collective behavior in alloy formation, it is imperative to develop our knowledge of the structure and dynamics of the liquid state and their correlations prior to and during solidification or vitrification. Unlike crystalline systems where the atomic structures and dynamics are readily determined by neutron or X-ray scattering, information about liquid alloys from experimental studies is limited due to inherent reactivity and rapid rates of diffusion. Therefore, atomistic simulations, coupled with experiments to ensure the accuracy and statistical mechanics modeling to extend time and length scales, become important approaches for determining the structure and dynamics of liquids and identifying the underlying atomistic pathways and mechanism for the formation of stable and metastable phases from multicomponent liquids.

Based on this premise, we have recently initiated a multidisciplinary team approach to tackle this grand challenge. A principal goal of this project is to determine the properties of liquid metals and how these properties affect the formation kinetics of the low temperature structure. This includes the processes of nucleation, growth, and glass formation. Our approach includes *X-ray and neutron scattering*, *molecular dynamics simulations* using both classical and quantum mechanical forces (i.e., embedded-atom method (EAM), tight-binding (TB), and first-principles density functional theory (DFT)), *thermodynamical calculations* and *statistical mechanics modeling* of liquids and liquid→solid transformations. The experimental and theoretical techniques work together closely to tackle the complex problem of correlation and dynamics in metallic liquids as well as liquid→solid transformations, as demonstrated in the selected research highlights presented in this section.

Al and Al-based alloys have been selected as prototype systems in our initial studies based on the synergistic ability to develop EAM and TB potentials from *ab initio* calculations and experimental data. We use a variety of computational, analytical, and experimental techniques to predict and measure (a) atomic structure factors, $S(q)$, and the short-range order of liquids; (b) diffusitivities and dynamics of liquids; and (c) relevant thermodynamic and structural quantities for the equilibrium state of liquids, including supercooled liquids, and how these quantities relate to non-equilibrium processes that lead to the selection between the competing crystalline and amorphous structures.

Ultimately, the studies will be extended to more complex systems of interest once a more comprehensive understanding of the prototype systems has been achieved and the multidisciplinary approach has been well developed.

TECHNICAL HIGHLIGHTS
- High-energy X-ray diffraction (HEXRD) at the Advanced Photon Source (APS) 6-IDD beamline has been used to determine the structures of molten $Al_{1-x}Cu_x$ alloys ($0 \leq x \leq 1$) at temperatures nominally between 973 and 1473K, as well as liquid $Cd_{86}Yb_{14}$ and liquid $Al_{1-x}Ge_x$ alloys ($0 \leq x \leq 1$).

- Self-diffusion coefficients of the Cu in molten $Al_{1-x}Cu_x$ alloys (x=0.10, 0.17 and 0.25) were successfully determined from the peak widths of quasielastic cold neutron scattering spectra from at three different temperatures (973K, 1173K and 1373K).

- Temperature variation of the structure and microstructure of molten eutectic $Al_{1-x}Si_x$ alloys (x=0, 0.125 and 0.18) was determined by neutron diffraction and small-angle neutron scattering (SANS) at the Institute Laue-Langevin, Grenoble, France and by HEXRD at the APS 6-IDD beamline.

- Novel metastable phases resulting from rapid solidification of $Al_{1-x}Ge_x$ alloys by a melt spinning technique have been observed.

- A new theoretical method was developed for accurate calculation of liquid and solid free energies based on density functional theory. The method has been applied successfully to Al. The same method has also been used to calculate interfacial free energies at various hard sphere crystal-melt interfaces. The obtained results were found to show good agreement with simulations.

- The *p-T* and ρ-*T* phase diagrams of the Lennard-Jones system, and anisotropic interfacial free energy of the crystal-melt interface for Lennard-Jones and aluminum systems have been predicted using the theoretical methods developed within this project.

- Thermodynamic calculations have been performed to determine the T_0 curves for five simple eutectic binary alloys, i.e, *Al-Ge, Ag-Ge, Au-Ge, Al-Si* and *Au-Si,* and for Al-rare earth (RE) alloys with intermediate compounds, i.e., *Al-Gd, Al-Ce, Al-Nd, Al-Ho, Al-Dy* and *Al-Y*. The results showed that the glass forming composition of the Al-RE alloys is strongly correlated with the valley of the T_0 curves in the phase diagram, suggesting that restriction of material transport is a key factor governing the formation of glass in these systems.

- *Ab initio* MD simulations were performed for liquid Al_xGe_{1-x} with x= 0, 0.2, 0.4, 0.6, 0.8, and 1.0 and at the temperature of 1250K; liquid $Al_{88}Si_{12}$ in the temperatures from 898K to1298 K, and liquid *Al-Cu* at the eutectic composition. The results provide useful information for better understanding the local structures and diffusion behavior in these liquid alloys.

- Tight-binding Al and Ge potentials have been developed. Tight-binding molecular dynamics simulations were performed to study the structure and properties of liquid Al, Ge and Si. The simulation results are in very good agreement with experiments. Tight-binding potential for Al-Si and Al-Ge are under development.

- A new EAM potential for pure Al has been developed and molecular dynamics (MD) simulations have been performed to study the supercooled Al liquid. Classical MD simulations using three different EAM aluminum potentials were performed to calculate the solid-liquid interfacial free energy. Potentials for Cu and Al-Cu are under development.

- The phase diagram for the liquid-glass transition of a model density functional as function of the virial coefficients of the liquid has been determined by a dynamical mean field theory for self-generated glasses.

- A theory which relates the rheological properties of a liquid with its interaction

strength was developed and we are in the process to determine quantitative results. We have also initiated to develop more realistic calculations based on the density functional theory of liquids and develop computational tools to perform numerical simulations of model systems with uniform frustration, in parallel to these more analytic calculations**.**

- Dynamical heterogeneity in glass Al was studied by molecular dynamics simulations and statistical mechanics modeling. We demonstrate that dynamical heterogeneity in glasses is directly related to local structural properties (e.g., density) and that the slow diffusion in a highly viscous, glassy fluid is very similar in character to vacancy diffusion in crystalline solid and fundamentally different from Markovian diffusion in liquids.

INTERACTIONS WITH OTHER PROJECTS AND PROGRAMS

- The emphasis of this project on the relationship between the structure of the liquid and the formation of low-temperature phases naturally connects it to the Solidification Science Focus Area within the ME&P Program of the Ames Laboratory.
- Similarly, the structure and dynamics of the liquid are important in determining the glass formability of the metallic glasses being studied as part of the Science of Amorphous and Aperiodic Materials Focus Area. Also, the studies of thermodynamically properties (i.e., T_0 calculations) within this project would be useful for the Science of Amorphous and Aperiodic Materials Focus Area in designing of alloy compositions for new bulk metallic glass materials.
- Interactions with the theoretical efforts in the Condensed Matter Physics Program at the Ames Laboratory leading to electronic structure calculations, atomistic simulations (first-principles DFT and tight-binding molecular dynamics), and non equilibrium statistical mechanics modeling of liquids and glasses. As part of the current effort, we are attempting to provide a stronger theoretical link between the liquid structure

and the glass formability, in support of the experimental efforts in the other areas.

- This project is also in collaboration with J.R. Morris at Oak Ridge National Laboratory, involving atomistic simulations of liquid-solid interfaces and diffusion in liquid Al-Cu alloys.
- This project is also closely connected to the DOE's Computational Materials Science Network (CMSN) project on "Microstructural Evolution Based on Fundamental Interfacial Properties," Tony Rollett, David Srolovitz, Alain Karma, Principal Investigators.

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U. Dahlborg, M.F. Besser, M. Calvo-Dahlborg, G. Cuello, C.D. Dewhurst, M.J. Kramer, J.R. Morris, and D.J. Sordelet, "Structure of Molten Al-Si Alloys," *J. Non-cryst. Sol.* (in press).

Structure and Dynamics of Al-Cu Liquids

Personnel: M.J. Kramer (PI) D.J. Sordelet (PI), M.I. Mendelev (PI), M.F. Besser (Assistant Scientist)

Scope:

The study of liquid metals and alloys has drawn considerable attention recently, in particular due to the possibility of carrying out *ab initio* molecular dynamics (MD) simulations for these systems. Such simulations, in principle, can augment experiments and test models while providing insight into the dynamic behaviour of real materials. In order to facilitate our theoretical studies of the liquid state of metallic alloys, a series of experiments have been initiated to provide data necessary for validation of the MD simulations. Al-Cu liquid alloys are being emphasized because of their suitability for both X-ray and neutron diffraction, the latter including isotopic substitution of Cu.

Research Highlights:

1. Structure of Al-Cu Liquids: We have demonstrated very good correlations between high-energy synchrotron X-ray diffraction (HEXRD) and neutron diffraction data (NB. X-ray data acquisition rate is nearly 100 times faster than what is achievable using neutrons). This means that temperature variations in the liquid structures can be efficiently and accurately collected using HEXRD and 2-D area detectors. Mathematical corrections to the theta-dependent average structure factors and Compton scattering yield excellent agreement to $S(Q)$ results obtained with neutron diffraction from the same alloys, Figure 1.

HEXRD clearly distinguishes the composition-temperature variations in the $S(Q)$ of Al-Cu alloys, as illustrated in Figure 2, where it is seen that the scattering changes directly with increasing Cu content. The increased intensity of the low-Q portion of the $S(Q)$ data suggests longer-range clusters, while the development of a strong splitting in the second diffuse peak indicates the development of Al-Cu pairs. The loss of this diffuse peak with increasing superheat suggests a temperature dependence on the chemical short-range ordering in this alloy system that is also composition dependent.

2. Dynamics of Al-Cu Liquids: The most sensitive validation of theoretical predictions are made via comparison to the dynamic scattering function $S(Q,E)$ that is experimentally accessible via two complementary experimental techniques: neutron and high-energy X-ray inelastic scattering. However, the only direct determination of the self-diffusion coefficient is via quasi-elastic neutron scattering. Recently, we have determined the self-diffusion coefficient of Cu ions in molten Al-Cu alloys by measuring the width of quasi-elastically scattered neutron spectra obtained at the FOCUS time-of-flight spectrometer at the neutron spallation source SINQ in Switzerland. In the small Q region, the spectrum of quasielastically scattered neutrons, $S_{q.el.}^{inc}(Q,E)$, is interpreted in terms of a jump diffusion model for the atomic motions. In this model an atom is assumed to undrgo vibrational motion around an equilibrium
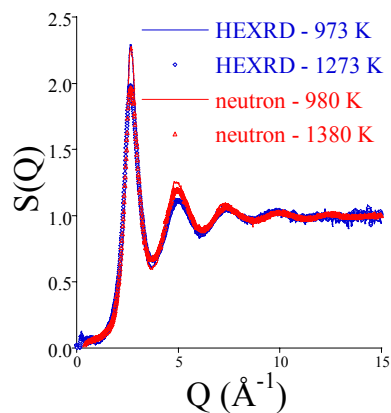

Fig. 1 Comparision of $S(Q)$ from high purity Al liquids at comparable temperatures using high energy photons and an area detector obtained in 300 s compared to 4.4×10^4 s for the neutrons.
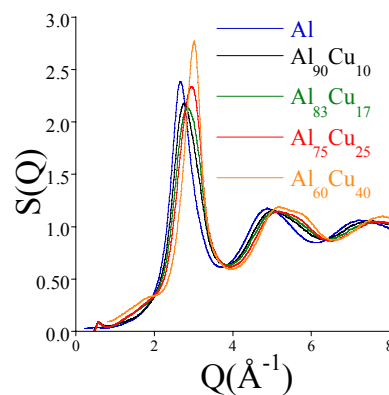

Fig. 2 S(Q) data taken on liquid Al-Cu alloys all at 973 K using HEXRD.

position during a time τ_0 and thereafter make a jump to another equilibrium position during the time τ_1. When $\tau_1=\tau_0$ the scattering function is of Lorentzian shape and is given by:

$$S_{q.el.}^{inc}(Q,E) = \frac{1}{\pi}\frac{\Delta E}{E^2 + (\Delta E)^2} \quad (1)$$,where at full width at half maximum $\Delta E = \frac{2\hbar}{\tau_0}\left[1 - \frac{e^{-2W}}{1 + Q^2 D \tau_0}\right] \quad (2)$

ΔE in the limit Q=0 equals $2DQ^2$, where D is the self-diffusion coefficient.

Using this method, selected Al-Cu alloys described in the preceding section were studied at 973K, 1173K and 1373K. A sample of eutectic composition containing the ^{63}Cu isotope was also measured to verify that the presence of coherently scattered neutrons in the measured spectra do not influence the determination of the diffusion characteristics. The FWHM values of all spectra showed a very good fit with Eq. 2, thus allowing for determination of the self diffusion constant D of Cu, as shown in Figure 3. At all compositions the temperature variation seems to be described by an Arrhenius law. A T^n temperature variation with n=2 has been invoked from MD simulations on pure elements. Taking into account the error in the determination of D, such a temperature variation cannot be excluded for these Al-Cu alloys. Comparison with MD simulations is in progress.
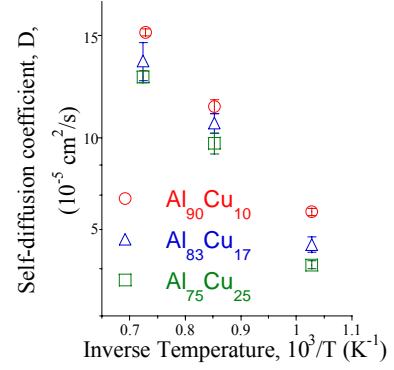

Fig. 3 Measured self-diffusion coefficients, D, for Cu in various Al-Cu alloys obtained from inelastic neutron scattering .

Significance:

The preceding experimental techniques are providing a broad picture of the effects of composition and temperature on the chemical and topological short-range order of liquid alloys. Specifically, the data are supporting the development of accurate inter-atomic potentials by M. I. Mendelev. For example, HEXRD and neutron diffraction data have been used to successfully develop a new potential for Al that resulted in an MD simulation that accurately predicted crystallization rather than glass formation upon cooling; the latter, unrealistic prediction is characteristic of previously existing inter-atomic Al potentials. MD simulations using emerging Al and Cu potentials are in progress to more realistically predict dynamic behavior compared to what is possible with *ab initio* MD simulations with limited numbers of atoms.

Impact:

Collectively these HEXRD and neutron scattering techniques provide the foundation to (i) test the accuracy of molecular dynamics simulations describing the structure and dynamics of liquid metals and alloys and (ii) support the development of highly accurate inter-atomic potentials that will facilitate more realistic MD simulations of liquid alloys.

Future Work:

Inelastic X-ray scattering studies have begun with H. Sinn from the Advanced Photon Source to achieve improved energy resolution compared to using neutrons.

Interactions:

J.R. Morris from Oak Ridge National Laboratory is performing *ab initio* simulations of diffusion in eutectic Al-Cu to calculate both tracer diffusion rates and dynamical structure factors. Inelastic neutron experiments are being performed with U. Dahlborg of the CNRS in Nancy, France.

Atomistic Simulations of Liquids

Personnel: C.Z. Wang (PI), M.I. Mendelev (PI), J.R. Morris (PI), K.M. Ho (PI), and S. Wang (Visiting Scientist)

Scope:

The scope of this effort is to obtain detailed knowledge about the structures and dynamics of liquids at the atomic scale. Molecular dynamics (MD) simulations are performed using interatomic forces ranging from first-principles density function theory (DFT), tight-binding (TB), to the classical embedded-atom method (EAM). The MD simulations are in close interaction with X-ray and neutron scattering studies in order to develop interatomic potentials for accurate description of the structures and dynamics of metallic liquid alloys. The simulations also provide input into thermodynamics and statistical mechanics modeling to study supercooled liquids and liquid-glass transformations.

Research Highlights:

We have performed *ab initio* MD simulations of liquid Al_xGe_{1-x} with x= 0, 0.2, 0.4, 0.6, 0.8, and 1.0 and at the temperature of 1250K, liquid $Al_{88}Si_{12}$ in the temperatures from 898K to1298 K, and liquid *Al-Cu* at the eutectic composition. The results from our simulations are compared with experimental data and provide useful information for better understanding the local structures and diffusion behavior in these liquid alloys. These simulation results also provide the database for development of TB and EAM potentials for these systems.

While *ab initio* MD is accurate, the computational workload is very heavy. Typically, it can handle liquid simulations with systems containing 100-200 atoms in a periodic unit cell. In order to increase our simulation capability to handle more atoms (about 1000 atoms) and at the same time retain the quantum mechanics description of interatomic forces, we are undertaking the effort to generate accurate environment-dependent tight-binding potentials for these systems. To date, tight-binding Al and Ge potentials have been developed. Using also the Si tight-binding potential developed previously, we have performed tight-binding molecular dynamics simulations to study the structure and properties of liquid Al, Si, and Ge as a function of temperature. The results obtained from the TBMD simulations agree well with X-ray and neutron scattering data as can be seen in Fig. 1. Development of tight-binding potentials for Al-Si, and Al-Ge systems are in progress.
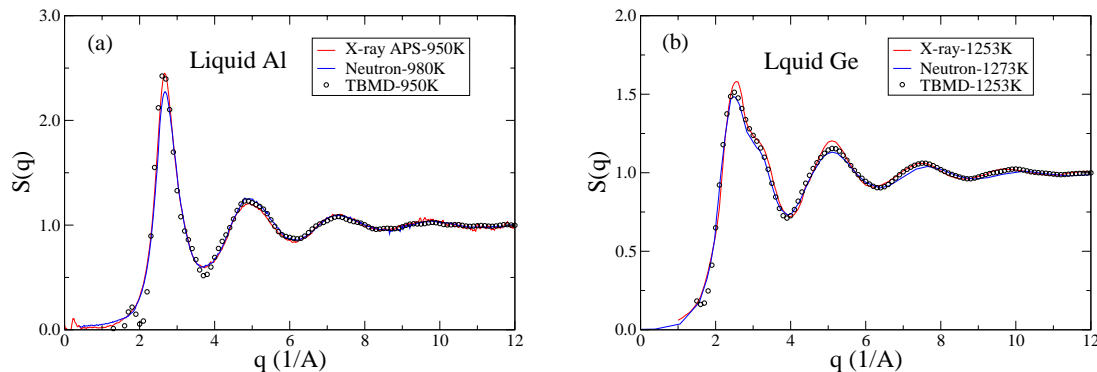

Fig. 1 Structure factor S(q) of liquid Al and liquid Ge obtained from TBMD simulations compare well with results from X-ray and neutron scattering experiments.

In order to extend our atomistic simulations to even larger length and time scales, we have also developed classical potentials based on the EAM scheme. We have developed a new EAM potential for pure Al and performed molecular dynamics simulations to study the supercooled Al liquid and liquid-solid interfaces. The properties predicted by the new potential are in very good agreement with available first-principles or experimental data. This new potential is also more accurate for describing liquid Al than other EAM potentials in the literature. Fig. 2 shows the change in the liquid structure upon heating. While these data were not included in the fitting procedure, the new potential almost exactly reproduces experimental data. Analysis of the solid-liquid interface properties shows that the potential provides the correct solid-liquid interface free energy and mobility (see the highlight in the Solidification Science Focus Area). Development of potentials for Cu and Al-Cu is in progress.
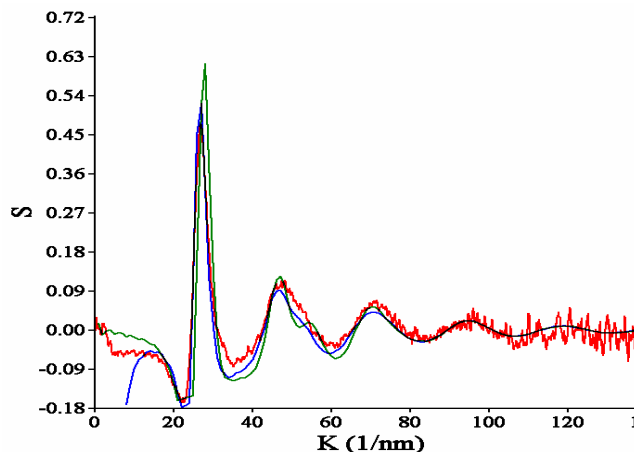

Fig. 2 The variation of the structure factor of Al when the temperature changes from 950 K to 1390 K: the X-ray data by M.J. Kramer (red line) and the data obtained from the molecular dynamics simulation with the EA (green line) and new (blue line) potentials.

Impact:

Information about liquid alloys, particularly the local structures, from experimental studies is limited due to the inherent reactivity and rapid diffusion of liquids. Therefore, atomistic simulations will provide useful information about the microscopic structures of liquids. In combination with statistical mechanics modeling to extend the time and length scales, atomistic simulations will play an important role in identifying the underlying atomistic pathways and mechanism for the formation of stable and metastable phases from multicomponent liquids.

Future Work:

We will continue to perform *ab initio* simulations of liquid Al-Cu. We will also perform *ab initio* molecular dynamics to study liquid Zr, liquid Pt, and molten Zr_xPt_{1-x} alloys to provide data for development of empirical potentials for molecular dynamics simulations of glass formation in Zr-Pt system. We will continue to develop the tight-binding potential and perform TBMD simulations for Al-Si, and Al-Ge liquid alloys. We will also develop a new empirical potential for Cu and Al-Cu and perform MD simulations for liquid Al-Cu alloys and solid-liquid interfaces in these alloys.

Interactions:

This solid-liquid interface simulation is closely connected to the Solidification Science Focus Area. The studies of supercooled liquids and liquid-solid transformations are also closely related to the studies in the Science of Amorphous and Aperiodic Materials Focus Area. The atomistic simulations bridge the experimental and thermodynamics and statistical mechanics modeling components within the liquid metal project by providing microscopic information for the statistical mechanics modeling and comparison with experiment. This study is also related to the DOE-CMSN project on "Microstructural Evolution Based on Fundamental Interfacial Properties."

Thermodynamical Properties of Metallic Systems

Personnel: X. Song(PI) and V. Warshavsky (Postdoc)

Scope:

A theoretical description of the free energies and correlation functions of hard sphere (HS) liquid and solid phases are developed using a fundamental measure density functional theory. Within the framework of Weeks-Chandler-Andersen perturbation theory, free energies of liquid and solid phases with any interaction potential can be obtained from these characteristics of the HS system within a single theoretical description. Application to the Lennard-Jones system and metallic systems yield liquid-solid coexistence results in good agreement with the ones from simulations. Such a strategy to treat the liquid and solid phases on the same footing also gives accurate interfacial properties of a liquid and solid interface.

Research Highlights:

Monte Carlo (MC) or Molecular Dynamics (MD) simulations can yield accurate results for free energies, but still are time-consuming processes. Perturbation theoretical approaches to the calculations of free energies in fluids and solids present an attractive alternative. One of the most reliable perturbation theories for free energy calculations was developed by Weeks, Chandler and Anderson (WCA) for liquids, which can also be extended to solids. In the framework of WCA theory the free energy is separated into two contributions: one being the free energy of an appropriate reference system and the second being the perturbative part. In general, a hard-sphere (HS) system with an appropriate HS diameter is chosen as the reference system, and the correlation function of that HS system is also utilized in the perturbation calculations. In such a treatment the key properties of the HS reference system can be obtained from MC or MD simulation results. For example, HS radial distribution functions of liquid and solid phases, as shown in Figs. 1 and 2, are parameterized using simulation data, so are the HS free energies of liquid and solid phases. Such a strategy is quite successful for a single component system, but the parameterization of multi-component systems will become extremely demanding and current theoretical approaches such as integral equations, do not yield results as accurate as simulations. In the present work we have developed a unified theoretical approach of calculating the free energies of liquid
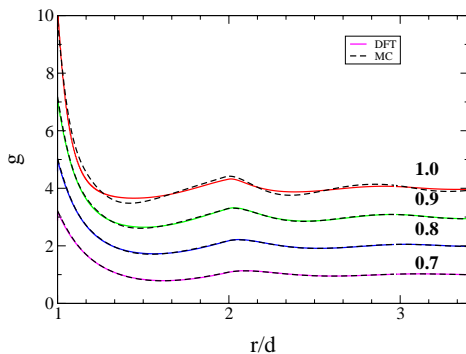

Fig. 1 Pair distribution function g(r) of liquid at densities 0.7(purple), 0.8(blue), 0.9(green), 1.0(red). The solid line is the result of our theory, the dashed line is the result of MC simulations. For clarity, curves for densities at 0.8,0.9,1.0 are shifted upwards by 1,2,3, accordingly.
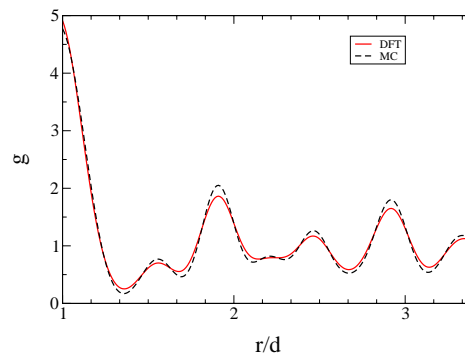
Fig. 2 Pair distribution function g(r) for solid at effective density1.05. Solid line corresponds to the result of the present theory. Dashed line is the Monte Carlo results

and solid phases using a fundamental measure density functional theory. Namely, we can obtain the properties of liquid and solid phases for an HS reference system within a single theoretical framework (see Table 1 and Figs. 1-3). At the same time, our approach can be generalized to multi-component systems since the fundamental measure density functional theory is known to provide accurate results for hard sphere mixtures. We have also applied this theoretical framework to the calculation of interfacial free energies between liquid-solid interfaces of the hard sphere systems. The calculated interfacial free energies are found to be in good agreement with simulat

Table 1. Excess free energy per particle for the Lennard-Jones system obtained from MC simulations and the present theory at effective temperature 2.74.

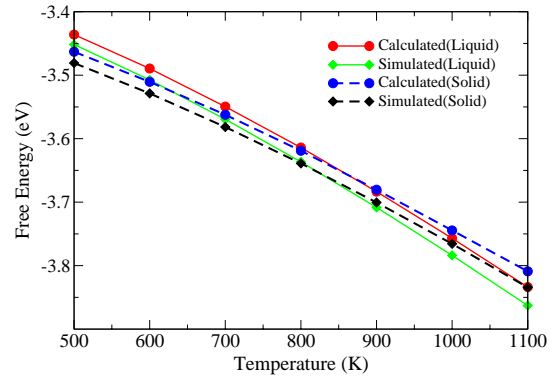| Density	MC simulations	This work
Liquid		
0.2	-0.04	-0.03
0.4	-0.01	0.005
0.7	0.38	0.36
0.8	0.65	0.63
0.9	1.05	1.02
1.0	1.58	1.56
1.1	2.31	2.27
Solid		
1.2	3.138	3.162
1.3	4.074	4.052
1.4	5.31	5.19
1.6	9.01	9.04
1.8	14.91	14.95
2.0	23.74	23.79
2.4	53.63	53.69

Fig. 3 The free energies of liquid and solid aluminum from Mei-Davenport EAM potential using perturbation theory and computer simulations. Circles connected with solid/dashed line are from our calculations of the liquid/solid phase free energy. Diamonds connected with solid/dashed line are from simulations of the liquid/solid. phase free energy.

Impact:

Free energy is an important thermodynamic parameter of condensed matter systems. If the dependence of free energy on temperature and the bulk density is known, many other thermodynamic quantities of the system, such as chemical potential, pressure, compressibility, can be calculated. The general theoretical strategy to calculate free energies, interfacial free energies and phase behaviors will open the door for a direct comparison between theory and experimental measurements. The phase behaviors will offer guidance for the search of new materials and the interfacial free energies will have a direct impact on the understanding of solidification processes.

Future Work:

Extension to multi-component systems is currently underway and the great advantage of our approach will become much more apparent in comparison to computer simulations. Also, we plan to extend our approach to the calculation of time-dependent quantities, such as diffusion coefficients and interfacial mobilities, which will impact our understanding on non-equilibrium processes.

Interactions:

Our work serves as a bridge between the potential development part of this overall effort and the experimental measurement of phase behavior of metallic systems. Our interfacial free energy calculations can also be compared with direct experimental measurement so that a reliable theoretical methodology for the thermodynamic properties of metallic systems can be developed.

Determining the Crystal-melt Interfacial Free Energy

Personnel: J.R. Morris (PI), X. Song (PI), and M.I. Mendelev (PI)

Scope:

We have used molecular dynamics simulations of coexisting crystal and liquid phases of a number of monatomic systems to extract out the interfacial free energy and its dependence on the interface orientation by examining the fluctuations of the interface. The interfacial free energy anisotropy is small, but plays an important role in solidification dynamics. The interfacial free energy is also important for the nucleation rates, within classical nucleation theory. Results for model systems give good agreement with other calculations performed independently. For Al, there is a significant sensitivity to the interatomic potential, related to the structure of the liquid. This results in different nucleation behavior of the systems.

Research Highlights:

Our method uses coexistence simulations, as shown in figure 1 on the right. Colors indicate the crystalline order, with red being the least. The calculation of the order parameter allows us to determine the height of the interface. The interface between the crystal and liquid phases is rough, and fluctuates on the molecular dynamics time scale. The height fluctuations are related to the interfacial stiffness by

$$\left\langle \left| h(q) \right|^2 \right\rangle = \frac{kT}{\tilde{\gamma} q^2} \qquad (1)$$

where the interfacial stiffness is given by

$$\tilde{\gamma}(\theta) = \gamma(\theta) + \gamma''(\theta) \qquad (2)$$

Fig. 1 Coexisting liquid and crystal simulations for examinng interfacial

and $\gamma(\theta)$ is the anisotropic interfacial free energy. The approach uses the fact that the interfacial stiffness is more anisotropic than the interfacial free energy, allowing for the free energy and its anisotropy to be accurately determined.

An excellent test of this approach was performed for the Lennard-Jones system, where independent calculations by R. Davidchack and B. Laird were performed, using an entirely different approach. The results are shown in Table 1. As can be seen, the results are in excellent agreement. The interfacial free energies agree within 3%; note that several years ago, factors of two disagreements were common. The two

All values in units of (ε/σ^2)	Current work (JCP 2003)	Davidchack & Laird (JCP 2003)
(100)	0.375(8)	0.371(3)
(110)	0.366(8)	0.360(3)
(111)	0.357(8)	0.347(3)
(100)-(110)	0.009(2)	0.011(4)
(100)-(111)	0.018(2)	0.024(4)

Table 1. Interfacial free energies for the Lennard-Jones system, compared with independent calculations.

approaches can each resolve the small anisotropy between the different interfaces. However, the present technique is more sensitive to the anisotropy; thus, the error bars given in the table are *smaller* for the
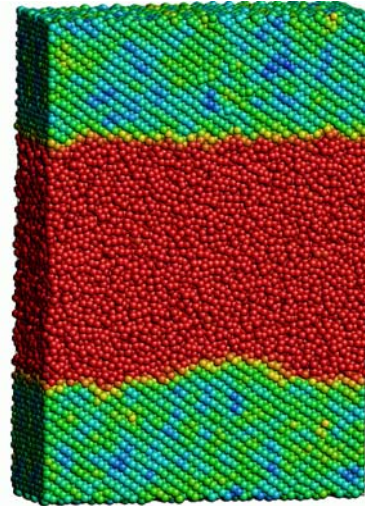
differences than for the original value, in contrast with the results of Davidchack and Laird, which give more accurate results for the *average* value but less accuracy for the differences.

We have also applied the method using three different Al potentials, including one developed by one of us (MIM), to determine the sensitivity to interatomic potential. The three potentials all had reasonable melting temperatures (within 1-2% of the experimental value), making for an easier comparison. The results for the stiffness are shown in figure 2` as a function of angle relative to the (100) interface rotating about the [001] direction. As can be seen, the Ercolessi and Adams potential gives a significantly higher stiffness (and free energy) than the other two potentials. The other two potentials give values close to 100 meV/Å^2, in reasonable agreement with nucleation data. These two potentials produce liquid structures closer to the experimental values (as determined by both X-ray and neutron diffraction), while the Ercolessi & Adams potential gives a more "icosahedral" liquid structure.
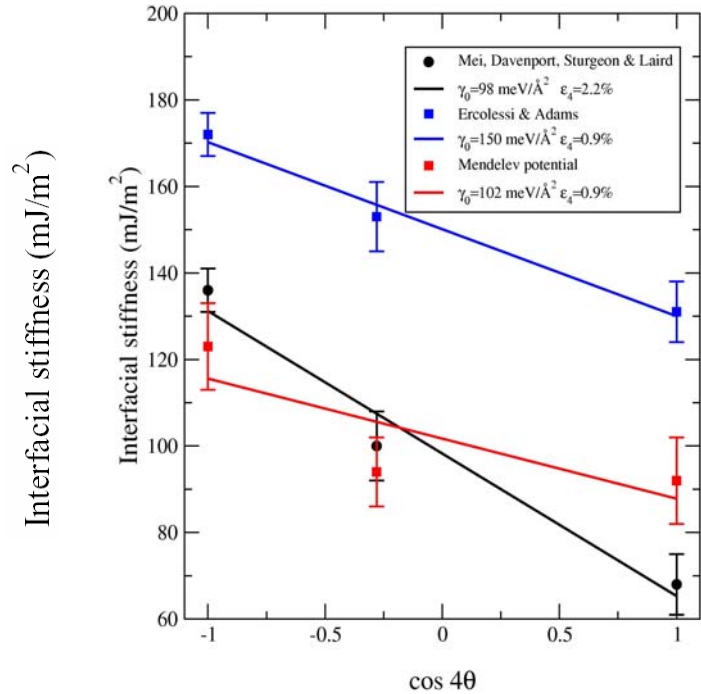

Fig. 2. Interfacial stiffness vs. orientation, showing the anisotropy and the strong dependence on interatomic potential

Impact:

This work shows the importance of liquid structure (and its dependence on interatomic potential) in determining the interfacial free energy. It clearly demonstrates the importance of testing interatomic potentials and it is significant a step towards understanding the behavior in important Al-based alloys.

Future Work:

Work is continuing to develop potentials for Al-Cu, to determine how alloying changes the interfacial free energy. Ab initio simulations of Al-Cu are being performed to examine the chemical ordering and the structure in the liquid state, as a test of potentials. X-ray scattering and neutron studies of liquid structure and dynamics of Al-Cu will provide detailed tests of the potential, and new insight into the dynamics of the alloy liquid.

Interactions:

This work is continuing in collaboration with James Morris in the Alloy Behavior and Design project at Oak Ridge National Laboratory.

Thermodynamic Limits of Crystallization
and the Prediction of Glass Formation Tendency

Personnel: K.M. Ho (PI), R.E. Napolitano (PI), C.Z. Wang (PI), M.J. Kramer (PI), and Y.X. Yao (Student)

Scope:

The scope of this effort is to understand the thermodynamic and kinetic implications leading to the glassy state exhibited by many metallic systems. A principal aspect of this effort involves the development of criteria for glass-formation in metallic systems through the study of T_0 temperatures within the alloy phase diagram.

Research Highlights:

Metallic alloys which resist crystallization in their undercooled states sufficiently well to become amorphous solids or "metallic glasses" have emerged as a very interesting and potentially useful class of materials. However, the criteria for glass-formation in metallic systems are still poorly understood. Experimental investigations have focused on alloy systems with deep eutectics, where the liquids are stable at lower temperatures. Unlike traditional topological or network glass systems where structural frustration promotes the formation of the glass state, metallic glasses are currently only found in multicomponent alloy systems. This indicates that restriction of material transport might be important in the glass formation process. In the scenario of restricted material transport in the liquid, the thermodynamic stability of the liquid towards crystallization is different from usual phase diagrams where it is assumed that there is always enough time for the material to separate into regions of different compositions. Indeed in many cases, the compositions for metallic glass formation do not coincide well with the eutectic composition but have a tendency to shift away from that composition.

The minimum degree of undercooling that is thermodynamically necessary for the diffusionless transformation of a liquid alloy to a solid solution, for a given alloy composition, is expressed by the T_0 curve in the phase diagram. For any given composition in an alloy, T_0 is defined as the temperature at which the liquid phase and the crystalline phase have equal Gibbs free energies. In this case, the intersection between the glass-formation temperature, T_g, and T_0 curves for the two (or more) crystalline phases involved in a eutectic reaction would indicate a reasonable composition range for glass formation. Therefore, the T_0 temperature may provide a reasonable upper limit for glass formation in a given alloy. However, very few quantitative estimates of T_0 curves have so far been reported.

We have calculated the T_0 curves for selected binary systems using the CALPHAD (CALculation of PHAse Diagrams) method with some missing parameters generated by *ab initio* calculations. Results have been obtained for five simple eutectic binary alloys: Al-Ge, Ag-Ge, Au-Ge, Al-Si and Au-Si .We found that a common and interesting feature is that the valleys of the T_0 curves are far away from the corresponding eutectic points as one can see from Fig. 1 for the case of Al-Ge. The calculations predict the composition of 40-50% of Ge, rather than the 28% of Ge at eutectic composition, should have stronger tendency for glass formation. Experiments using spin-melt technique are in progress to verify the theoretical predictions.
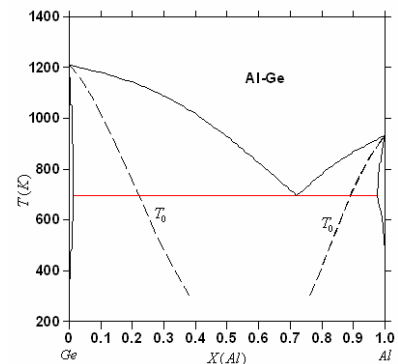

Fig. 1 Phase diagram of Al_xGe_{1-x} including the T_0 curves from our calculations

We have also performed the calculations for several Al-rare earth (RE) binary alloys and compared the results with reported observations of glass formation. The results show that the glass-forming compositions of the Al-RE alloys strongly correlate with the valleys of the T_0 curves in the phase diagram as can be seen from Fig. 2. The agreement of the predicted composition range for glass formation with the observed glass formation compositions indicate that restriction of material transport is a key factor governing the formation of glass in these systems, where relaxation to the energetically favorable crystalline state becomes sufficiently sluggish to effectively prevent its existence. This behavior differs substantially from the more common oxide glasses, where directional bonding constraints may lead to static glassy network structures from simple topological considerations.
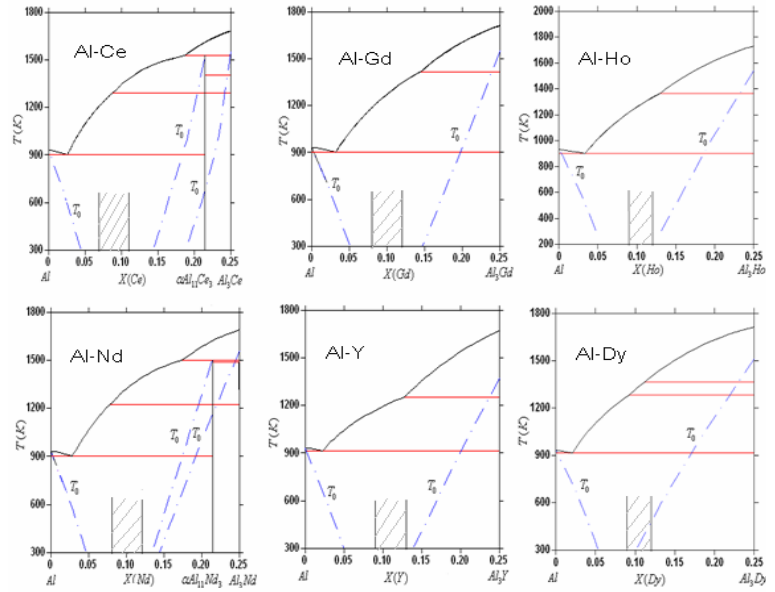

Fig. 2 Phase diagrams of Al-RE including the T_0 lines from our calculations. The shaded areas indicate the glass forming compositions observed in experiments.

Impact:

We suspect that the kinetic factors leading to glass formation in Al-RE alloys might equally applicable to many more metallic alloy systems. Ultimately, our analysis will be useful in guiding the design of alloy compositions for new bulk metallic glass materials.

Future Work:

While the T_0 calculations can help to identify the composition and temperature range for metallic glass formations, the liquid→glass transition is also strongly dependent on the cooling rate, relative to the intrinsic relaxation time of the alloys. Future work will be extended to study the relaxation time in liquid metallic alloys as a function of composition and temperature. The T_0 calculations will also be extended to include more elements beyond binary alloys.

Interactions:

This study is closely connected to the Solidification Science Focus Area and the Science of Amorphous and Aperiodic Materials Focus Area. Some predictions of glass-formation compositions will be checked by both experimental groups. The *ab initio* total energy calculations and free energy calculations efforts within this project will facilitate the T_0 calculations when information is not available from the CALPHAD database. Diffusion constants from *ab initio* or tight-binding MD simulations will also be used to understand kinetics relevant to metallic glass formation.

Glass Formability of Liquids

Personnel: J. Schmalian (PI), M.I. Mendelev (PI,) C.Z. Wang (PI), K.M. Ho (PI), and J. Willson (Student)

Scope:

The scope of this effort is to understand the conditions under which metallic liquids vitrify and to characterize the structure, dynamics and correlations of the glassy state. The two main research thrusts of this effort are: i) molecular dynamics simulations using an embedded atom potential for Al that yields very slow, glassy dynamics if sufficiently super-cooled and allows to investigate the dynamical heterogeneity in the glassy regime and ii) replica density functional calculations that allows to systematically study glass formability for model systems and for systems with realistic inter-particle potentials.

Research Highlights:

i) *Molecular dynamics simulations using an embedded atom potential for Al*: In this study, we used the Ercolessi-Adams (EA) potential. While we were able to show that this potential has several shortcomings in the description of the liquid structure of Al, we also demonstrated that it may serve as a model potential for the study of vitrification in one-component systems. We performed molecular dynamics simulations with this potential between 300 and 1400K. Below 800K we found that the characteristic time scales of the problem become considerably larger compared to the high temperature liquid (which exists as a concurrent phase, depending on the initial conditions in the simulation, down to 600K). While the pair correlation function of the glassy and the liquid states display only minor differences (see Fig. 1), the dynamics of both states is quite different. This can be seen in Fig. 2 where we show the displacement distribution for both states. The diffusion in the glassy regime characterized by a vibrational peak (i.e. particles oscillate around their random positions) resembles much more the vacancy diffusion of crystalline solids than ordinary Brownian motion with only short term memory. A transfer of spectral weight from this vibrational peak to jumps by one or two nearest neighbor distances occurs, again a behavior different from the liquid where a Gaussian peak is gradually shifted to larger distances obeying a diffusion law. The strong tendency towards vitrification and the occurrence of a split of the second peak in the pair distribution function are interesting in view of numerous proposals where such a split peak was related to local icosahedral correlations in metallic glasses. Analyzing the spatial correlation of the most mobile particles, we find a considerable spatial correlation of such mobile objects. In addition we were able to demonstrate that there is a strong correlation between the local particle density and the mobility of particles. These results demonstrate that dynamical heterogeneity in glasses is directly related to local structural properties (like density) and that the slow diffusion in a highly viscous, glassy fluid is very similar in character to vacancy diffusion in crystalline solid and fundamentally different from Markovian diffusion in liquids.
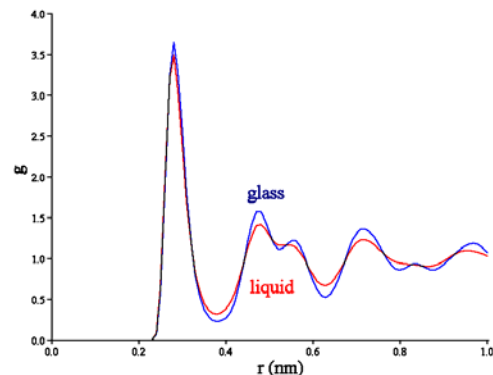

Fig. 1 Pair correlation functions of the glassy and liquid states at T=670 K and p=0 (the densities are different).
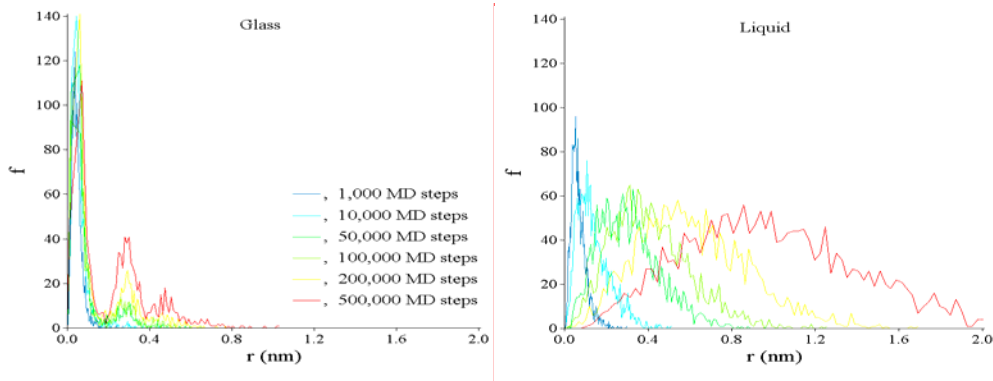
Fig. 2 The displacement distribution at T=600 K at the glassy and liquid states.

ii) *Replica density functional theory of glass formability*: We developed in collaboration with Gabriel Kotliar (Rutgers University) and Peter G. Wolynes (University of California) a dynamical mean field theory for self-generated glasses which is based on the density functional approach of liquids but properly takes into account the long time correlations of a frozen-in non-equilibrium glassy state. Here we successfully combined several approaches of strongly interacting many body physics: i) dynamical mean field theory which has recently revolutionized our understanding of interacting quantum systems; ii) the density functional approach of classical liquids, which allows to determine the equal time structure factor of a system in its liquid state; and iii) non-equilibrium statistical mechanics which allows one to deal with the additional long-time correlations of the glass. We also addressed the issue of the stability of a frozen state with respect to crystallization. All these results were obtained for a simple model system, the so-called Brazovskii model for micro-phase separation, and for liquids characterized by a realistic structure factor. In particular we analyzed vitrification for a system with EA-embedded atom potential.
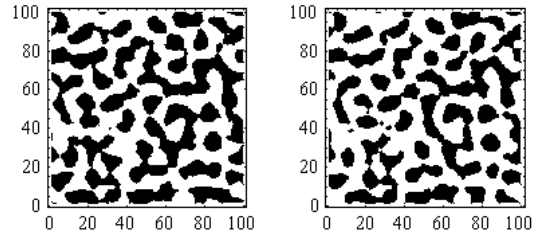

Fig. 3 Frozen density configurations for micro-phase separation at two distant times.

Impact:

Our results are of great relevance for a better understanding of structure, dynamics and correlations in glasses. Using realistic model potentials our very general approach allow us to make specific predictions for the correlation between density fluctuations and dynamical heterogeneity in metallic glasses.

Future Work:

Generalization to multi-component systems, allowing a detailed comparison with experiments.

Interactions:

There is a close interaction with essentially all efforts of the metallic liquids effort. This study is also closely connected to the Solidification Science Focus Area and the Science of Amorphous and Aperiodic Materials Focus Area within the ME&P program at Ames Laboratory.