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An Interatomic Potential for Studying CuZr Bulk Metallic Glasses**

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Binary alloys capable of forming metallic glasses have been discovered recently.^[1–8] The mechanical properties of BMGs are remarkably different from the ones of ordinary metallic alloys due to the atomic level disorder in the glassy state. Unlike crystalline materials plastic deformation in metallic glasses cannot be caused by lattice defects but takes place through atomic-scale deformation events and may furthermore involve localization through formation of shear bands. For understanding the origin of their mechanical properties it is important to get the basic understanding of fundamental theoretical problems through atomistic simulations.

Molecular dynamics (MD) treats atomic systems according to Newtonian mechanic laws. Atoms are point particles, interacting through an interatomic potential, describing the energy of an atom as a function of the positions of all atoms in a neighboring region of space. The time evolution of the system is obtained by numerically integrating Newton's second law. Often the interatomic potential is a classical potential, no quantum mechanical description of the material is attempted,

but the functional form of the potential may be derived from quantum mechanical arguments.^[9] MD is able to treat systems with millions of atoms, and permits the average calculations of transport (diffusion, thermal conductivities, viscosity), or mechanical quantities (elastic constant, plastic yield), and also the modeling of complex phenomena (shear band localization, fracture appearance, neutronic cascades).

The quality of the results will depend on the quality of the interatomic potential, simple potentials giving a less accurate description of the interatomic interactions while allowing very large simulations, more complicated potentials may give a better description of the interaction, but limit the simulation size. Many-body potentials such as the Embedded Atom Method^[10] and the Effective Medium Theory (EMT)^[11,12] have been shown to give a good description of the late transition metals crystallizing in close-packed structures, and their alloys, while still allowing simulations with millions of atoms.^[13] In this paper, we create an EMT potential optimized for modeling the mechanical and thermodynamic properties of CuZr bulk metallic glass.

CuZr was recently discovered to be a binary bulk metallic glass.^[6,14] Since binary alloys are easier to model than alloys with more elements, this makes CuZr an attractive bulk metallic glass to study theoretically. Previously, an interatomic force field has been fitted to CuZr by Duan *et al.*,^[28] but we find that the EMT force field described here provides a better description of the structure of the metallic glass. The potential developed here will be used to model the mechanical properties of CuZr, to be published elsewhere.

Fitting an Effective Medium Theory Potential

The functional form of EMT is described by Jacobsen *et al.*^[11] and will not be repeated here, as it is rather complex. The energy of each atoms is the sum of two terms, the *cohesive energy* and the *atomic-sphere correction*. The cohesive energy approximates the energy of an atom with the energy of an atom in a perfect face-centered cubic (FCC) crystal with the same electron density. Each atom contributes to the local electron density in its neighborhood with an exponentially decaying density. Two EMT parameters describe this contribution to the electron density: n_0 describes its magnitude, and η_2 is the inverse decay length. The energy of an atom is then a function of the electron density at its positions, this function has a minimum determining the equilibrium lattice constant. The EMT parameters s_0, λ and E_0 describes the position of this minimum, the curvature, and the depth, respectively. The atomic-sphere correction handles departures from the reference FCC structure. It is described as the difference between

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Table 1. Properties used in fitting the potential. Elastic constants are in $\text{\AA}/\text{eV}^3$, energies are in eV/atom and lattice constants are in \AA . All values for CuZr refers to the B2 structure. The first five values (for pure Cu) were not used in the fitting in this work, but are provided for reference. All values for Zr and CuZr are obtained with DFT calculations, except the Zr [16] and CuZr cohesive [17,18] energies, which are experimental.

Property	Optimized value	Target value	Difference
Cu Shear Modulus ($\text{eV}/\text{\AA}^3$)	0.511	0.511	0.000
Cu Bulk modulus ($\text{eV}/\text{\AA}^3$)	0.889	0.886	0.003
Cu C11 ($\text{eV}/\text{\AA}^3$)	1.09	1.10	-0.01
Cu Cohesive Energy (eV)	3.52	3.51	0.01
Cu Lattice Constant (\AA)	3.58	3.61	-0.03
Zr Shear Modulus ($\text{eV}/\text{\AA}^3$)	0.141	0.150	-0.009
Zr Bulk modulus ($\text{eV}/\text{\AA}^3$)	0.474	0.440	0.034
Zr Cohesive Energy (eV)	6.30	6.30	0.00
Zr Lattice Constant (\AA)	4.57	4.55	-0.02
CuZr Shear Modulus ($\text{eV}/\text{\AA}^3$)	0.306	0.276	0.03
CuZr Bulk modulus ($\text{eV}/\text{\AA}^3$)	0.667	0.751	-0.084
CuZr Formation Energy (eV)	-0.139	-0.140	0.001
CuZr Lattice Constant (\AA)	3.19	3.28	-0.09

a pair potential in the actual structure and the same pair potential in the reference structure. This pair potential is also an exponentially decaying function, the EMT parameters V_0 and κ describe the strength and inverse decay length. The atomic-sphere correction term is responsible for a system's resistance to shear.

EMT does *not* contain special parameters for describing the interactions between unlike atoms in an alloy, instead these interactions are described by combining the potential parameters for the elements. For example, the cohesive energy of a Cu atom surrounded by Zr atom will depend on the Cu parameter describing how the energy of the Cu atom depends on the local electron density (s_0 , λ and E_0), and on the Zr parameter describing how this density decays near the Zr atom (n_0 and η_2).

We fit the seven parameters relating to Zr, while keeping the Cu parameters fixed to the values obtained in a previous work on the CuMg metallic glass.^[15] We do the fitting by minimizing an error function

$$f(\{p\}) = \sum_i q_i \cdot |C_i^{\text{EMT}}(\{p\}) - C_i^{\text{target}}|^2 \quad (1)$$

where $\{p\} = \{s_0, n_0, E_0, V_0, \eta_2, \lambda, \kappa\}$ is the list of parameters that need to be fitted, q_i are normalizing constants, C_i^{EMT} and C_i^{target} are the EMT values (obtained from molecular dynamics) and target values (from experiment or from DFT calculations), respectively. The sum goes over the different properties used to fit the potential, such as lattice constants, cohesive energies and elastic constants for Cu, Zr and the CuZr alloy in the B2 (or CsCl) structure, see table 1.

Table 2. EMT parameters.

Parameter	Cu	Zr
s_0 (\AA)	1.41	1.78
E_0 (eV)	-3.51	-6.3
λ (\AA^{-1})	3.693	2.247
κ (\AA^{-1})	4.943	3.911
V_0 (eV)	1.993	2.32
n_0 (\AA^{-3})	0.0637	0.031
η_2 (\AA^{-1})	3.039	2.282

The target values were obtained from quantum mechanical calculations using Density Functional Theory within the generalized gradient approximation (DFT-GGA), using the Perdew-Wang 91 exchange-correlation functional^[19] and ultrasoft pseudopotentials. Calculations were performed with the dacapo program from the CAMP Open Software project.^[20] The usual care was taken to ensure convergence with respect to plane wave cutoff (350 eV), number of k-points ($8 \times 8 \times 8$) etc.

For fitting the interatomic potential parameters we use a Nelder Mead simplex method^[21] for optimizing the Function 1 described above. The method requires only evaluations of the functions and not their derivatives for finding the minimum of more than one independent variable.

The result of the fit is shown in Table 1, showing how well the target values were fitted, and Table 2 showing the resulting EMT parameters for Cu and Zr.

Testing the Potential

Before using the potential obtained in the previous sections, it is important to test its ability to predict properties not used in the fitting procedure. Since the intended application

Table 3. Comparison between DFT and EMT results for different crystal structures for $\text{Cu}_{50}\text{Zr}_{50}$. The B2 structure was used in the fitting of the potential, the other structures are tests of the potential.

Structure		E (eV/atom)	V (\AA^3 /atom)
$\text{Cu}_{50}\text{Zr}_{50}\text{B1}$	(DFT-GGA)	0.275	19.57
	(EMT)	0.203	18.60
$\text{Cu}_{50}\text{Zr}_{50}\text{B2}$	(DFT-GGA)	-0.1202	17.64
	experiment ^[17]	-0.14	—
$\text{Cu}_{50}\text{Zr}_{50}\text{L1}$	(DFT-GGA)	-0.035	17.23
	(EMT)	-0.0011	17.23
$\text{Cu}_{50}\text{Zr}_{50}\text{L1}_1$	(DFT-GGA)	0.250	18.01
	(EMT)	-0.1295	18.25

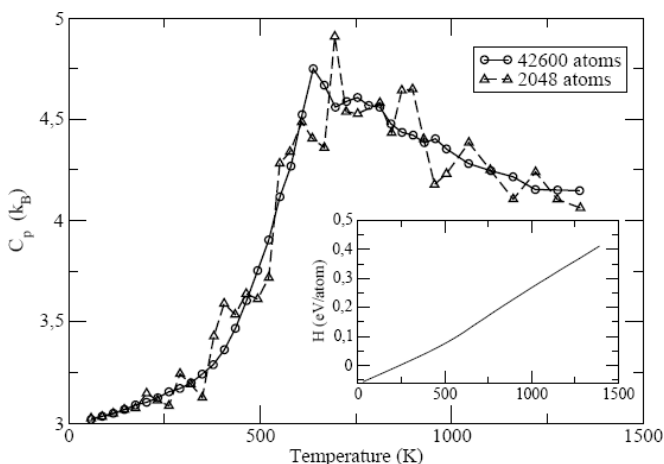


Fig. 1. Specific heat vs. temperature for two different sizes of CuZr metallic glass system during annealing. Inset: Enthalpy versus temperature for the 2048 atoms system.

is CuZr metallic glasses, the potential is both tested on ordered alloys with the same composition, and on thermodynamical and structural properties of the metallic glass.

The first test consists of comparing the formation energies and lattice constants (here expressed as a volume per atom) for four different ordered alloys. These structures do not exist in nature; the B2 (or CsCl) structure is the stable crystal structure for $\text{Cu}_{50}\text{Zr}_{50}$. However, the other structures can be set up in the computer, and the energies and lattice constants can be compared to more accurate DFT calculations. The results are given in Table 3. If the potential is able to describe low-energy ordered structures, it is likely to correctly describe the local structures occurring in a metallic glass as well. All the structures except the L1_1 structure are well described. The L1_1 structure consists of alternating close-packed layers of Cu and Zr, this structure is presumably far from what one will encounter in metallic glasses, and the inability to reproduce that formation energy is not too worrying.

A more relevant test is to examine how this potential performs when used on a metallic glass. We therefore prepared a CuZr metallic glass in order to compare the glass transition temperature and the short-range order as measured by the radial distribution function to experiment.

We performed MD simulations in order to obtain the CuZr glass phase from the melt. We used two different systems sizes, starting from body-centered cubic crystals with 2048 and 42600 atoms, and the sites randomly occupied by Cu and Zr. The resulting glassy systems were cube-shaped with side lengths of 3.3 nm and 9.1 nm, respectively. The systems were cooled from 1400 K (well above the melt temperature) in steps of 25 K, with an average cooling rate of 0.54 K/ps. Each temperature step begins with a short period of Langevin dynamics^[22] to thermalize the system to the new temperature, followed by a simulation with constant (N,P,T) dynamics, using a combination of Nosé-Hoover and Parrinello-Rahman dynamics.^[23,24] The prethermalization with Langevin dynamics is necessary to prevent oscillations in the temperature

otherwise seen when the temperature of a Nosé-Hoover simulation is changed abruptly. During the constant (N,P,T) dynamics we recorded averages of different quantities of interest like pressure, volume, kinetic and potential energy of the system, in order to perform the thermodynamics analysis.^[15] The simulations were performed using the ASAP program from the CAMP Open Software project.^[20]

When plotting the enthalpy versus temperature (inset of Fig. 1), we observe a change in the slope near 600–700 K which indicates the glass transition. From this slope the heat capacity vs. temperature (Fig. 1) can be determined. The change in the heat capacity indicates the glass transition, T_g . We extracted the glass transition temperature by taking the centered derivative of $C_p(T)$ and choosing the maximum.^[15] T_g was estimated to be 620 K, compared to the experimental value of 670 K.^[25] This good agreement is encouraging, in particular when one considers that no data on glasses and no thermodynamical data at all was used to fit the potential.

The radial distribution function analysis (RDF) is a standard method for obtaining information about the structure of the systems, especially for liquids and amorphous structures. In Figure 2 we show partial RDF functions $g_{\text{Cu-Cu}}$, $g_{\text{Cu-Zr}}$, $g_{\text{Zr-Zr}}$ at the glass transition temperature. The first peaks of the RDF indicate the average distance at which we find nearest neighbor atoms ($g_{\text{Cu-Cu}}$ and $g_{\text{Zr-Zr}}$ yields the distance between like atoms, $g_{\text{Cu-Zr}}$ the distance between unlike atoms). By integrating the RDF functions until the first minimum, we obtain the number of nearest neighbors atoms for Cu and Zr atoms. The results are summarized in Table 4 with comparison with other experimental and simulations data. The values for the coordination numbers and the interatomic distances are in good agreement with the experimental ones, although the interatomic distances are slightly underestimated, and the CuZr coordination number is slightly overestimated. The differences are, however, no larger than the differences between the different experiments.

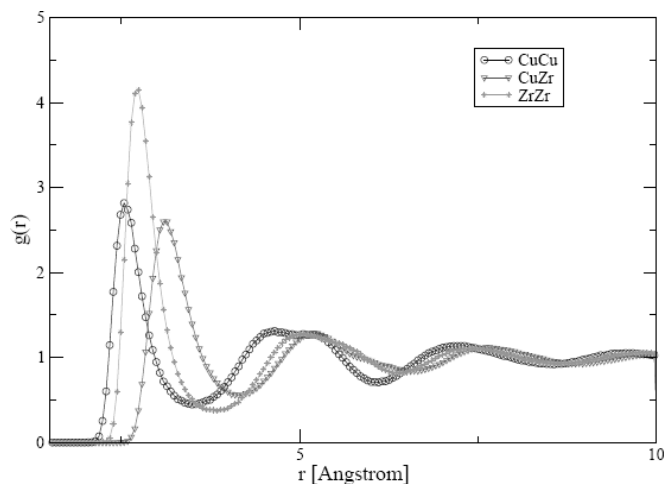


Fig. 2. Radial distribution function for CuZr metallic glass.

Table 4. Average nearest neighbor distances and coordination numbers. The first line is this work, the two next are experimental data with two different methods. The last line is simulations by Duan et al. with another potential and a slightly different composition. Since Cu and Zr are present in unequal amounts, the number of Zr neighbors to a Cu atom is different from the number of Cu neighbors to a Zr atom, and two numbers are therefore given for N(CuZr).

Composition	Method	R(Å) CuCu	R(Å) CuZr	R(Å) ZrZr	N CuCu	N CuZr	N ZrZr
Cu ₅₀ Zr ₅₀	This work	2.56	2.75	3.13	4.44	6.24	7.59
Cu ₅₀ Zr ₅₀	EXAFS ^[26]	2.57	2.84	3.19	4.1	5.4	7.4
Cu ₅₀ Zr ₅₀	XRD ^[27]	2.68	2.80	3.16	4.6	4.8	7.8
Cu ₄₆ Zr ₅₄	Simul. ^[28]	2.67	2.78	3.22	3.2	7.6/7.5	9.1

As a final test, we have compared the bulk and shear modulus with experimental values. Our calculated values were obtained at zero temperature by applying strain in the elastic limit and relaxing the structure each strain step. We find 108.69 GPa and 29.25 GPa, respectively, compared to the experimental values 101.2 GPa and 31.3 GPa.^[25] The deviation is less than 8%.

Conclusion

An EMT interatomic potential was fitted for CuZr, with the purpose of simulating the CuZr bulk metallic glass. The potential was fitted to lattice constants, cohesive energies and elastic properties of elemental Cu, elemental Zr and Cu₅₀Zr₅₀ in the B2 crystal structure. The fitted potential does a reasonable job of reproducing lattice constants and energies of other structures of Cu₅₀Zr₅₀. When a glassy sample of Cu₅₀Zr₅₀ is produced, we find a glass transition temperature, elastic constants and structural data in form of average coordination numbers and average nearest neighbor interatomic distances in good agreement with experiment.

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