Computational Structure Refinement by Hybrid Reverse Monte Carlo Simulation Incorporating Fluctuation Electron Microscopy

Jinwoo Hwang[1, 2], Z. H. Melgarejo[2], Y. E. Kalay[3, 4], M. J. Kramer[4], D. S. Stone[2], and P. M. Voyles[2]

[1.] Materials Department, University of California, Santa Barbara, CA 93106-5050, USA
[2.] Department of Materials Science and Engineering, University of Wisconsin, Madison, WI 53706, USA
[3.] Department of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, 06800 Turkey.
[4.] Ames Laboratory (DOE), and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, USA

In many glassy systems, nanoscale medium range atomic order (MRO) is related to important properties, such as the glass transition and structural relaxation. Experimentally observing MRO, however, is often difficult because of the elusiveness of the order embedded in a disordered matrix. Fluctuation electron microscopy (FEM) measures the structural fluctuations caused by MRO in glass [1]. Structural fluctuations are measured by the normalized variance, V, amongst many STEM nanodiffraction patterns [Fig. 1(a)] as a function of scattering vector magnitude, k, and the STEM probe size, R.

$$V(k, R) = \frac{\langle I(k, R, \mathbf{r})^2 \rangle_{\mathbf{r}}}{\langle I(k, R, \mathbf{r}) \rangle_{\mathbf{r}}^2} - 1, \qquad (1)$$

where I is the diffraction intensity, and $\langle\ \rangle_{\mathbf{r}}$ indicates averaging over position on the sample, $\mathbf{r}$. Stronger diffraction from MRO increases I at a certain k, creating a peak in $V(k)$. Some intuitive interpretation of FEM data is possible because the k position of peaks in $V(k)$ carries information about the internal structure of MRO. For more complicated systems, however, the interpretation becomes more difficult.

We developed a hybrid reverse Monte Carlo (HRMC) simulation to interpret the FEM data from Zr-Cu-Al metallic glass [2]. Our HRMC combines the χ^2 match between experimental and simulated $V(k)$, and an embedded atom model (EAM) potential [3]. The total χ^2 is

$$\chi^2 = E + \alpha \sum_i \frac{\left(\beta V_s(k_i) - V_e(k_i)\right)^2}{\sigma^2(k_i)}, \qquad (2)$$

where E is the EAM energy, V_s and V_e are the simulated and experimental variances, respectively, and σ is the uncertainty in V_e. The derivations of the proportionality factor, α, and the correction factor for the Stobbs factor and sample thickness, β, are described in Hwang et al. [2]. Minimizing χ^2 insures a structural model in good agreement with experiment from short to medium range length scales, and results in a more realistic structure compared to a model refined against the EAM energy only [3] or RMC models [4] with only conventional diffraction data, which is not sensitive to MRO [1].

HRMC using FEM data from as-quenched and three annealed $Zr_{50}Cu_{45}Al_5$ glass samples showed good fits in all four cases [Fig 1(b)]. Calculated $V(k)$ from the EAM only model did not show

any peaks, indicating that it does not contain realistic MRO. Using Voronoi polyhedra analysis of the HRMC models, we found two new types of MRO, crystal-like MRO with pseudo 6-fold symmetry, and aligned icosahedral MRO with 2-fold symmetry (Fig. 2). The crystal-like MRO is abundant in the as-quenched model, but gradually changes into aligned icosahedral MRO as the structural relaxation progresses in the annealed models. Our results provide new insights into the structural origins of the glass transition and the relaxation of metallic glasses.

References

[1] M. M. J. Treacy et al., *Rep. Prog. Phys*. **68**, 2899 (2005).
[2] Jinwoo Hwang et al. *Phys. Rev. Lett*. **108**, 195505 (2012).
[3] Y. Q. Cheng, E. Ma, and H. W. Sheng, *Phys. Rev. Lett*. **102**, 245501 (2009).
[4] H. W. Sheng et al., *Nature* **439**, 419 (2006).
[5] This work is supported by the National Science Foundation under Contract No. CMMI-0824719 and by Teragrid Grant No. DMR-100061.
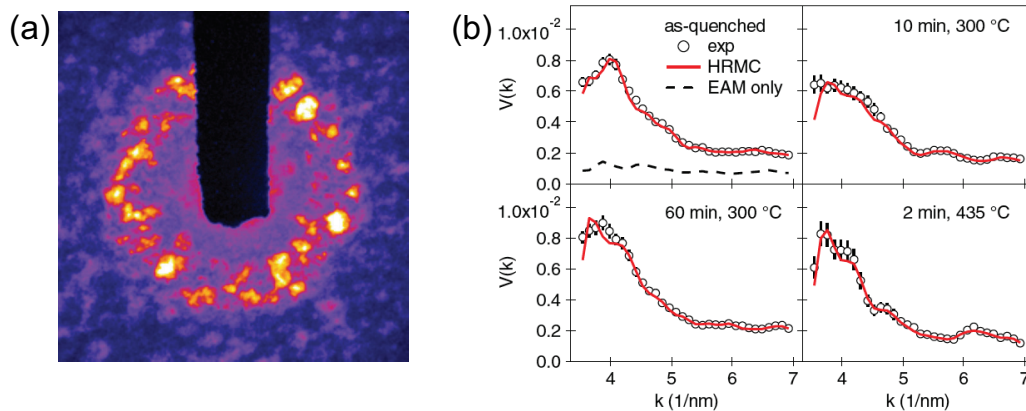
Fig. 1. (a) Example nanodiffraction pattern from metallic glass with $R = 2$ nm (b) Experimental $V(k)$ from the as-quenched and annealed samples and simulated $V(k)$ from the models. Calculated $V(k)$ from EAM only model is also shown for comparison.
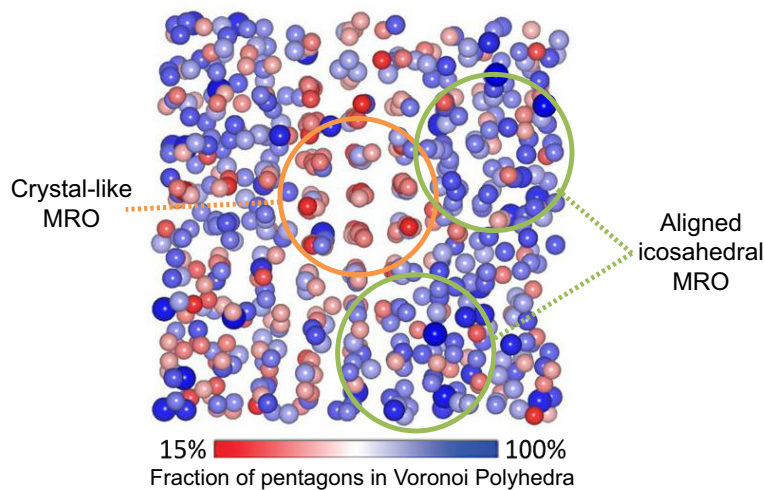

Fig. 2. A region of the annealed $Zr_{50}Cu_{45}Al_5$ HRMC model including crystal-like and aligned icosahedral MRO. Atoms are colored by the fraction of pentagons in their Voronoi polyhedra.