

# First-principles simulation of supercooled liquid alloys

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## Abstract

Accurate simulation of multicomponent alloys demands a first-principles approach because empirical potentials become increasingly inaccurate and difficult to develop with each additional constituent element. In contrast, the computational difficulty of simulating an alloy from first principles remains essentially independent of the number of elements. However, equilibration times increase with the number of elements, regardless of the choice of interaction, owing to the need for longer-range diffusion to adequately sample configuration space. The difficulty is exacerbated at low temperatures because of the rapid decline of diffusion constants. Here we discuss the application of replica exchange molecular dynamics to aid equilibration of supercooled alloys, and we also mention the possibility of Hamiltonian exchange molecular dynamics to accelerate equilibration at high temperatures.

(Some figures in this article are in colour only in the electronic version)

## 1. First-principles molecular dynamics simulation

In a multicomponent alloy of  $N_e$  distinct elements,  $N_e(N_e + 1)/2$  combinations of elements interact pairwise. The number of distinct interactions grows even faster if three-body and higher interactions are included. Small quantitative errors in any of the interactions can lead to large qualitative errors in predictions for outcomes such as pair correlation functions. The likelihood of a satisfactory description of an alloy diminishes as  $N_e$  grows large. There is a pressing need to simulate structures containing many elements because of alloy systems such as superalloys and bulk metallic glasses (figure 1) that contain as many as  $N_e = 9$  different constituents.

Fortunately first-principles methods exist [1, 2] that are more accurate than interaction potentials even for a single element and for which the computational difficulty remains nearly constant as the number of elements grows. The disadvantage of first-principles methods is that the time required for the simulation is large and grows roughly as the third power of the total number of atoms,  $N_a$ , unlike interaction potentials for which order- $N_a$  methods are common. This limits typical simulation sizes to  $N_a < 300$  and limits typical run lengths to a few picoseconds.

The limitation on run length is especially problematic for multicomponent alloys because equilibration and sampling become more difficult as  $N_e$  increases. There are two chief difficulties. First of all, generation of a highly independent configuration requires elements diffuse a distance of order their typical separation within the sample (see figure 1). If one element is present at low concentration this distance may be large, and diffusion times grow as the second power of distance. Secondly, if there are many elements there are many possible local structures, requiring correspondingly longer times to sample important configurations. While these difficulties are present for first-principles simulations and empirical potentials alike, they are a greater impediment for first-principles simulations owing to the limitations on run length.

## 2. Replica exchange method

Diffusion is faster at high temperatures because the rate to cross an energy barrier varies as  $\exp(-\Delta E/k_B T)$ . The replica exchange method [4–6] exploits the relatively fast diffusion at high temperatures to accelerate the sampling of independent configurations at low temperatures. The concept is illustrated

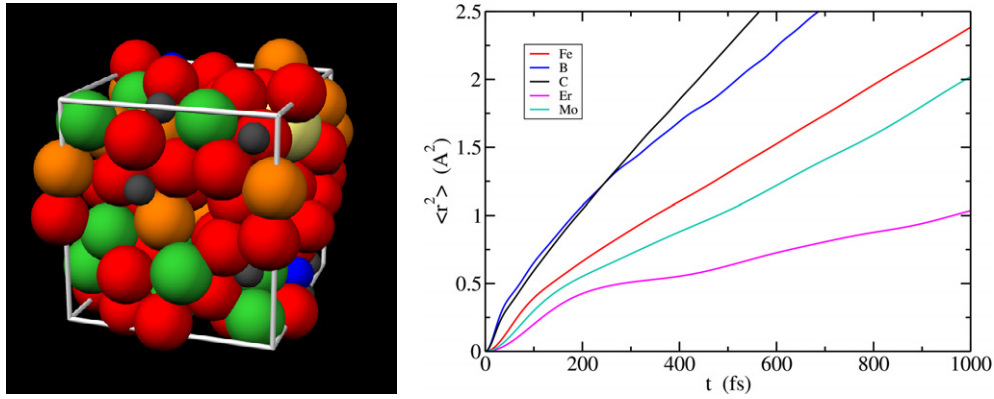
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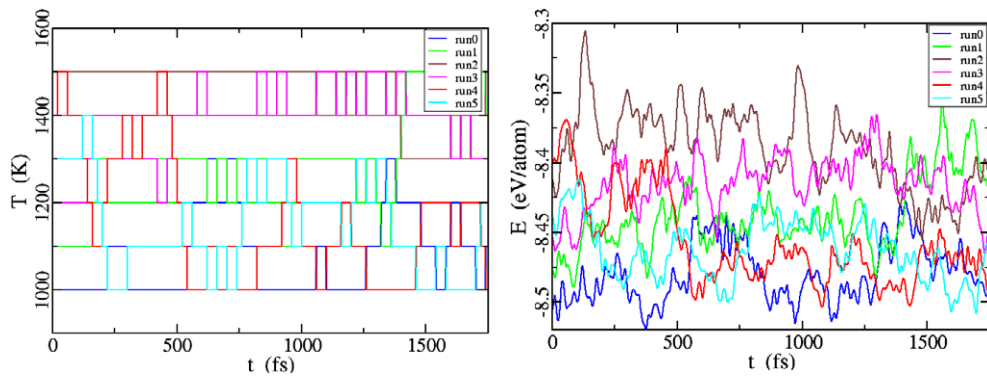
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**Figure 1.** Left: Representative structure of a 6-component bulk metallic glass  $\text{Fe}_{48}\text{B}_6\text{C}_{15}\text{Er}_2\text{Mo}_{14}\text{Cr}_{15}$  [3]. The color coding (online) is Fe (red), B (blue), C (gray), Er (yellow), Mo (orange), Cr (green). The simulation cell has periodic boundary conditions and edge length approximately 10 Å. Right: Diffusion plots for  $\text{Fe}_{63}\text{B}_6\text{C}_{15}\text{Er}_2\text{Mo}_{14}$  at  $T = 2000$  K.



**Figure 2.** Left: Swapping of temperatures among independent runs. Right: Energy fluctuations of each run. Shown is an actual tempering run of duration 1800 fs for the alloy  $\text{Fe}_{48}\text{B}_6\text{C}_{15}\text{Er}_2\text{Mo}_{14}\text{Cr}_{15}$  utilizing temperature range  $T = 1000$ – $1500$  K.

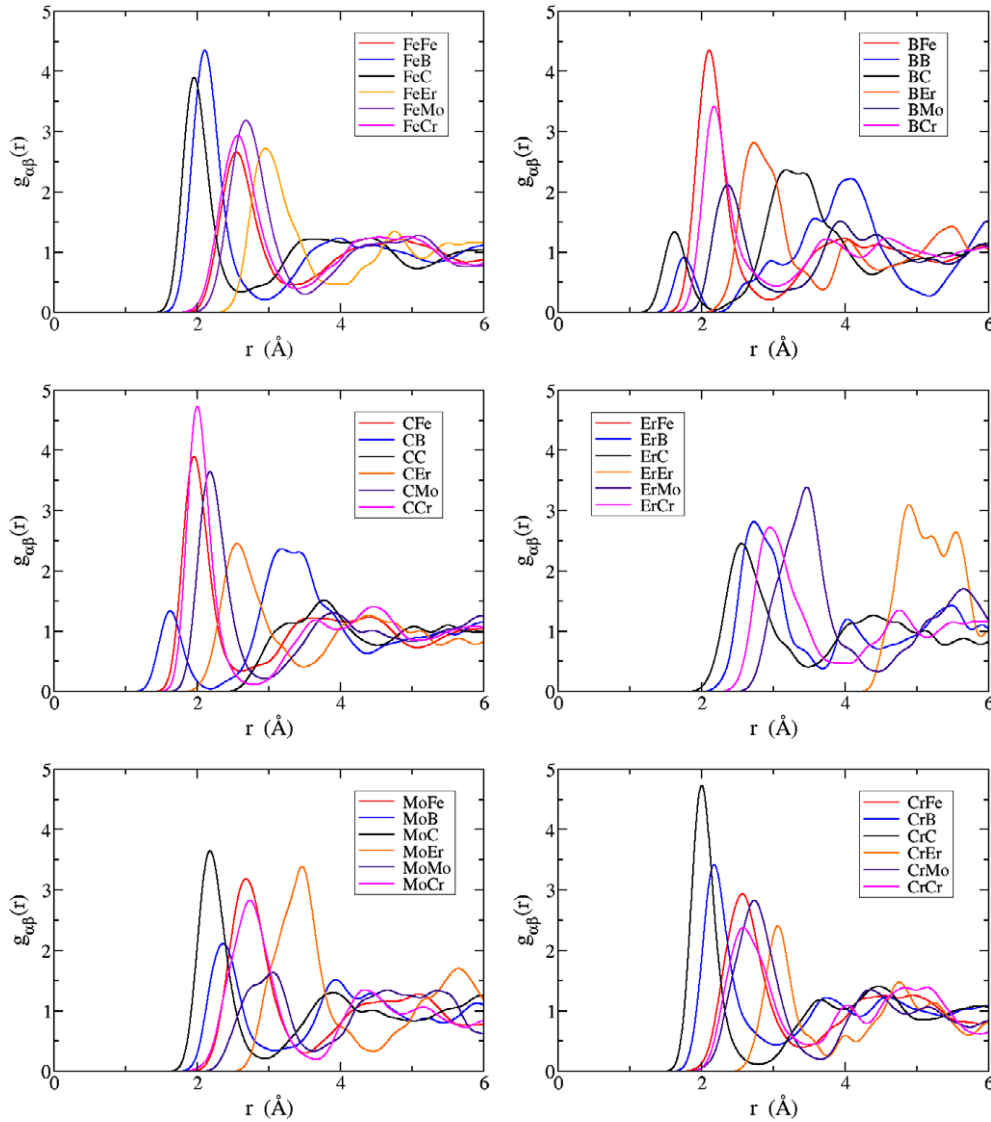
in figure 2. Here a run means a time series of configurations evolving from a single initial condition. While a run is held at fixed temperature its energy fluctuates over time. Consider a pair of runs  $i$  and  $j$ , currently at temperatures  $T_i$  and  $T_j$  with instantaneous configurations  $C_i$  and  $C_j$  at energies  $E_i$  and  $E_j$ . The probability for any configuration  $C$  of energy  $E$  to occur in the equilibrium ensemble at any temperature  $T$  is proportional to  $\exp(-E/k_B T)$ . Hence we could swap the configurations  $C_i$  and  $C_j$  between temperatures  $T_i$  and  $T_j$ . If we carry out the swap with probability  $\exp(\Delta E \Delta \beta)$  where  $\beta = 1/k_B T$ , the equilibrium ensemble probabilities will be preserved at  $T_i$  and  $T_j$ . Only the dynamics (time evolution) will be affected, because runs  $i$  and  $j$  continue new temperatures.

In figure 2 swaps are attempted between runs at adjacent temperatures every 20 fs. Over time the temperature of a given run rises and falls in temperature, providing fresh independent configurations at low temperatures generated by the molecular dynamics at higher temperatures. We can achieve deep supercooling by extending this method to lower temperatures. To maintain high swap acceptance rates we take smaller temperature intervals at low temperatures. A good independent set of initial conditions is crucial for runs of this length, as the diffusion of runs between low and high temperature is not particularly fast. This particular simulation would benefit from extending to twice the time.

In figure 3 we show well-equilibrated partial pair correlation functions at  $T = 1000$  K obtained from this simulation by disentangling the time series of temperatures to collect configurations specific to each temperature, then average the distribution function over this set. One can also collect histograms of structural energies at each temperature, then reconstruct the temperature-dependent free energy [7].

### 3. Hamiltonian exchange method

Although the replica exchange is helpful we are still limited by the atomic diffusion rates at our highest temperature. Adding additional runs at still higher temperatures can be effective. However an alternative method [8, 9] results in vastly improved dynamics at high temperatures. The idea is to carry out a pair of high temperature runs, one using first principles for relatively short durations and the other using approximate classical potentials for long durations. Consider a pair of configurations, one obtained from first principles and the other from the classical run. Let  $\Delta E_C$  be the energy change for the swap evaluated with classical potentials, and let  $\Delta E_Q$  be the energy change evaluated from first principles. We can swap the configurations between classical and quantum runs with probability  $\exp(-(\Delta E_C + \Delta E_Q)/k_B T)$  and bring the



**Figure 3.** All partial pair correlation functions at  $T = 1000$  K for the replica exchange run on  $\text{Fe}_{48}\text{B}_6\text{C}_{15}\text{Er}_2\text{Mo}_{14}\text{Cr}_{15}$  illustrated in figure 2.

benefits of fast classical dynamics to the quantum simulation without altering the equilibrium ensembles. Of course, the equilibrium ensemble of the quantum simulation differs from the classical simulation, even though they are at the same temperature, because the classical potentials provide an imperfect description of the energetics.

Achieving this goal requires classical potentials of sufficient quality that an acceptably high swap rate is achieved. If the classical potentials were perfect, then  $\Delta E_C = -\Delta E_Q$  and the swap rate would be 1. We started the paper by pointing out the difficulty of producing accurate classical potentials. However, our method actually does not require *very* accurate potentials, especially if the swaps are performed at high temperatures so that the energy errors are not large compared with  $k_B T$ . We created pairwise interaction potentials for Fe–B and Fe–B–C–Mo by fitting energy and force data to an empirical oscillating form. These potentials yielded swap acceptance rates of 0.7 for  $\text{Fe}_{80}\text{B}_{20}$  and 0.5 for  $\text{Fe}_{65}\text{B}_6\text{C}_{15}\text{Mo}_{14}$  at  $T = 1500$  K. The result is a larger sample of independent

configurations for our quantum simulation at  $T = 1500$  K than could have been obtained by conventional molecular dynamics. The acceleration is by several orders of magnitude, limited primarily by the attempted swap frequency.

We will use this supply of highly independent  $T = 1500$  K configurations to increase the sample diversity of our replica exchange molecular dynamics and improve the sampling of the low temperature equilibrium ensemble.

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