Force-biased Monte Carlo and *ab initio* modeling of transition metal clusters

A force-biased Monte Carlo (FMC) method, based on the Finnis-Sinclair and the Sutton-Chen potentials, was used to model the putative ground-state structure of the transition-metal clusters of Fe, Ni and Cu with sizes of 13, 30 and 55 atoms. Specifically, the total energy of the clusters was minimized using the local gradient of the potentials in Monte Carlo simulations. The atomic structure of the FMC clusters was analyzed and compared with their counterparts from the Cambridge Cluster Database (CCD) upon relaxation of the clusters with the plane-wave module in density-functional-theory code NWCHEM. Additional comparisons between the FMC and CCD clusters were based on the pair-correlation function, the bond-angle distribution, the coordination number of the first-coordination shell, and the Steinhardt bond-orientational order parameter, which provide information about the two- and three-body correlation functions, the local environment of the atoms and the geometry of the clusters. An atom-by-atom comparison of the FMC and CCD clusters was conducted by superposing one set of clusters onto another, and the electronic properties of the clusters were addressed by computing the density of electronic states by constructing DFT Hamiltonians.

We used *ab initio* MD simulations, coupled with geometry optimization using the DFT in the generalized-gradient approximation (GGA), to predict the putative ground state of 13-atom Fe, Cu and Ag clusters. An extensive search of competitive candidate structures from the *ab initio* potential-energy surface indicates that a low-symmetry bilayer structure is the most probable candidate for the ground-state structure of Fe_{13}, Cu_{13} and Ag_{13} clusters. Such representative structures of putative global minimum of Fe_{13}, Cu_{13} and Ag_{13} are shown in the photo gallery section of this web site. A comparison with a number of bilayer structures, optimized with numerical pseudo-atomic orbital basis (employed in the DFT-based SIESTA package) and plane-wave basis (in VASP), indicates that the resulting putative global-minimum configuration is essentially independent of the nature of basis functions. The work is based on our force-biased Monte Carlo method.