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Structure and energetics of nickel, copper, and gold clusters

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Abstract. The most stable structures of Cu_N, Ni_N, and Au_N clusters with $2 \leq N \leq 60$ have been determined using a combination of the embedded-atom (EAM), the quasi-Newton, and our own *Aufbau/Abbau* methods for the calculation of the total energy for a given structure, the structures of the local total-energy minima, and the structure of the global total-energy minimum, respectively. We have employed two well-known versions of the EAM: (1) the 'bulk' version of Daw, Baskes, and Foiles and (2) the Voter-Chen version which takes into account also properties of the dimer in the parameterization. The lower-energy structures (also for the smallest) of Cu_N and Ni_N clusters (i.e., structural details as well as symmetry) obtained with the two versions are very similar. Thus, our study supports an universality of the bulk embedding functions for copper and nickel. But for gold clusters the differences between structures calculated with the two different versions of the EAM are significant, even for larger clusters.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 36.40.-c Atomic and molecular clusters – 68.65.-k Low-dimensional, mesoscopic, and nanoscale systems: structure and nonelectronic properties – 31.15.Ct Semi-empirical and empirical calculations (differential overlap, Hückel, PPP methods, etc.)

1 Introduction

The fact that clusters have unique properties has been formulated in various ways, including 'small is different', 'for clusters the properties do not scale with the size', and 'every single atom counts'. In essence all statements imply that the properties of the clusters depend critically and in a complicated way on the number of atoms. The fact that any property depends first on the number of atoms and second on the structure of the cluster means that the determination of the structure for a given cluster is of ultimate importance for developing structure-property relations. Here, theoretical studies can be of importance. Unfortunately, geometry optimizations using ab initio methods are still computationally unfeasible for clusters with more than 10–20 atoms. It is possible to carry out ab initio calculations for clusters containing more atoms, but then only for a few fixed structures of high symmetry (see for example Ref. [1]). Consequently, information provided by empirical potentials is highly relevant, for instance in yielding candidate structures for subsequent first-principles calculations. However, the model potentials may be inaccurate. Therefore, it is important to understand the applicabilities and limitations of the model potentials before using them uncritically. With this objective we have studied clusters of three metals, Ni, Cu, and Au, using two different versions of the embedded-atom method in order to study system- and potential-specific as well as -independent properties. We shall here report results of this study where we have optimized, using an unbiased approach, clusters with up to 60 atoms.

For the present work it is important to mention that ab initio calculations on Ni_N, Cu_N, and Au_N clusters have been performed mainly for very small clusters [2–11] as well as on single, high-symmetric, larger ones [1]. On the other hand, many-body empirical potentials [e.g., the Gupta, Murrell-Mottram, Sutton-Chen, and embedded-atom method (EAM) ones] have been used in several studies to perform unbiased structure optimizations with almost no constraints on size or symmetry [12–29]. From earlier empirical studies on nickel and copper clusters [17,20,26–29] it was found that highly stable clusters occur for $N = 13$ and $N = 55$, for which the structures are multilayer icosahedra, i.e, the first and second Mackay icosahedra. Moreover, an *fcc* truncated octahedron was found to be the structure of the global total-energy minimum for Ni_{38} and Cu_{38} clusters. However, Kabir et al. [20] found a structure with icosahedral geometry for the Cu_{38} cluster.

The gold clusters seem, on the other hand, to have a complicated growth, possessing disordered minima for the energetically low-lying isomers [12,14–16,21]. Even for the geometry of the first magic-sized gold cluster, Au_{13}, there is still not full agreement: results obtained with first-principles calculations have given a disordered

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structure [2,8], while methods based on empirical many-body potentials have predicted the icosahedron as the most stable structure [13,17–19,26]. For the Au_{38} cluster empirical potentials [13,17–19,26] as well as first-principle calculations of Häkkinen et al. [7] have predicted the *fcc* truncated octahedron to be the most stable structure, while other studies have suggested the formation of either a disordered structure or amorphous low-lying isomers [14–16,21]. Similarly, recent experiments and calculations [12,14,16,21,30] suggest that Au_{55} possesses a low-symmetric structure.

Accordingly, in order to obtain further insight into the structures of the not-too-small metal clusters, it is highly important both to study the influence of the potential that has been used and to perform unbiased structure optimizations.

2 Method

In the present study the structure and energetics of the lowest-lying structures of Cu_N, Ni_N, and Au_N clusters with N up to 60 have been determined for each cluster size using a combination of the EAM (for the calculation of the total energy for a given structure), the variable metric/quasi-Newton method for the determination of the local total-energy minima, and our own *Aufbau/Abbau* method for the determination of the global total-energy minimum. We have employed two well-known versions of the EAM: (i) the 'bulk' version of Daw, Baskes, and Foiles (DBF) [31–33] and (ii) the Voter-Chen (VC) [34–36] version which takes into account properties of the dimer in the parameterization. In our very recent study [29] we have calculated the geometries of the four lowest-energy structures of Ni_N clusters with N up to 150 using the DBF potential. This study showed a very good agreement with experimental and other theoretical studies. Accordingly, it suggests that the bulk embedding functions and potentials for nickel are applicable also to smaller clusters with many low-coordinated atoms. Nevertheless, it is not obvious that the DBF EAM functions will describe accurately properties of other metal clusters. On the other hand, the main advantage of the Voter-Chen version of the EAM is the parameterization of the potentials also to dimer properties.

3 Results

First, we calculated the bond length of the dimers, Ni_2, Cu_2, and Au_2. Our results together with ab initio and experimental values of reference [38] are shown in Table 1.

The results show a good agreement with experiment for the DBF version of the EAM except for Au, where it fails completely. On the other hand, the VC version gives an overall very good agreement. This simple test suggests that the DBF version could provide proper geometries of Ni and Cu clusters even for the smallest cluster sizes, but may fail for small Au clusters.

Our further calculations confirm this statement. The left panels of Figure 1 show the difference between the average binding energies per atom calculated with the different potentials of the EAM as a function of cluster size. One can see that the agreement is very good for Cu, satisfactory for Ni, and poor for small gold clusters, but surprisingly good for all metals with $N > 20$.

Table 1. The calculated bond length (in Å) of the dimers in comparison with ab initio and experimental values. DBF and VC denotes the EAM versions of Daw, Baskes, and Foiles and of Voter and Chen, respectively.

System	DBF/VC	ab initio	exp.
Ni	2.13/2.22	2.17	2.20
Cu	2.15/2.23	2.17	2.22
Au	1.81/2.40	2.55	2.47

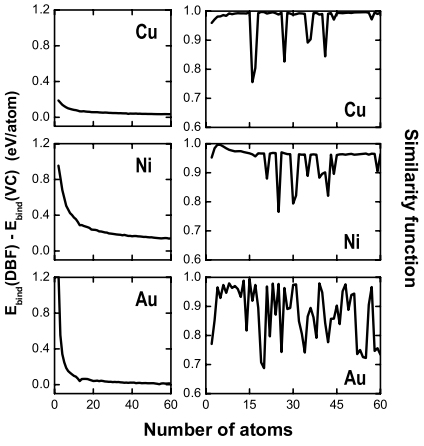

Fig. 1. Comparison between DBF and VC results: energetics and structure.

The concept of similarity functions, introduced by us in reference [28], turns out to be very fruitful. With these functions it is possible to quantify structural differences and similarities. Here, we use it as follows. In order to quantify whether the cluster of N atoms calculated using the DBF potentials is structurally related to that using the VC potential, we calculate and sort all interatomic distances, d_i, $i = 1, 2, \cdots, \frac{N(N-1)}{2}$, of each of the two clusters, separately. Subsequently, we calculate

$$q = \left[\frac{2}{N(N-1)} \sum_{i=1}^{N(N-1)/2} \left(d_i^{\mathrm{DBF}} - d_i^{\mathrm{VC}} \right)^2 \right]^{1/2}, \qquad (1)$$

where the superindex distinguishes between the two potentials. The similarity function is then

$$S = \frac{1}{1 + q/u_l} \qquad (2)$$

(we choose $u_l = 1$ Å) which approaches 1 (0) if the DBF cluster is very similar to (different from) the VC cluster.

The right panels of Figure 1 show these functions. It is easily seen that the structures of DBF and VC copper clusters are very similar, and only for four values of N some larger differences are observed. For nickel clusters we observe some more differences, although the agreement is nevertheless reasonable. The situation for gold is different. Here, the figure shows large differences for $N > 13$.

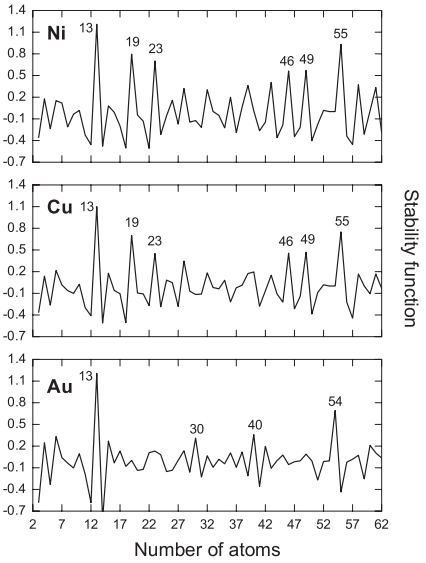

Fig. 2. The stability function (in eV) for Ni, Cu, and Au clusters as calculated using the VC potential.

Moreover, the similarity function approaches 1 only for few values of N.

A word of caution is, however, appropriate here. In our more detailed work on Ni_N clusters we calculated the four energetically lowest isomers for N up to 150 [29]. There we showed that there is a repeating cross-over between the different isomers, i.e., often the energetically lowest isomer for a certain value of N was structurally most similar to an energetically higher one for the Ni_{N-1} cluster. Moreover, the four isomers were indeed close in energy. Thus, marginal changes in the total energies (e.g., when replacing the DBF potential with the VC potential) may easily change the relative order of energetically close isomers and, accordingly, lead to a situation where the energetically lowest isomers of the two potentials are structurally quite different as, e.g., exemplified in the results of Figure 1 for Au.

Therefore, in order to obtain further information on the differences in the two approaches we show in Table 2 the point groups of the global-minima structures for the same systems as in Figure 1. The point symmetries for $2 \leq N \leq 13$ are not shown, as they are found to be identical for all three metals and both potentials. In accord with the results above, we find only 6 values of N for Cu where the two potentials lead to different symmetries, 9 for Ni, but 24 for Au. Moreover, in general we find the same ground-state symmetries for a given N for Ni and Cu, whereas that for Au is different.

More information on the similarities and differences between the three elements can be obtained through the stability function, defined as $E_{\rm tot}(N+1)+E_{\rm tot}(N-1)-2E_{\rm tot}(N)$, and shown in Figure 2, which has maxima for particularly stable clusters. Here we have considered only the VC potential. Also this figure confirms that Ni and Cu do not differ much, whereas the properties of Au are different.

In reference [29] we presented a number of different quantities that were explicitly constructed to give detailed but compact information on the structures of the different clusters as a function of N. Here, we shall use one further of those in analyzing the present results, i.e., the so-called radial distance. For a given cluster of N atoms we identify the center,

$$\boldsymbol{R}_0 = \frac{1}{N}\sum_{i=1}^{N}\boldsymbol{R}_i, \tag{3}$$

Table 2. Point groups of the optimized nickel, copper, and gold clusters for $14 \leq N \leq 60$.

	Ni	Cu	Au
N	DBF/VC	DBF/VC	DBF/VC
14	C_{3v}/C_{3v}	C_{3v}/C_{3v}	C_{2v}/C_{3v}
15	C_{2v}/C_{2v}	D_{6d}/D_{6d}	D_{6d}/D_{6d}
16	C_s/C_s	D_{3h}/C_s	D_{3h}/C_{2v}
17	C_2/C_2	T_d/C_2	T_d/T_d
18	C_s/C_s	C_s/C_s	C_{2v}/C_{4v}
19	D_{5h}/D_{5h}	D_{5h}/D_{5h}	C_{2v}/D_{5h}
20	C_{2v}/C_{2v}	C_{2v}/C_{2v}	C_s/D_{3d}
21	C_1/C_s	C_s/C_s	C_s/C_s
22	C_s/C_s	D_{6h}/D_{6h}	D_{6h}/C_1
23	D_{3h}/D_{3h}	D_{3h}/D_{3h}	C_2/C_{2v}
24	C_{2v}/C_{2v}	D_3/D_3	C_{3v}/C_2
25	C_{2v}/C_3	C_3/C_3	D_2/C_2
26	T_d/T_d	T_d/T_d	D_{3h}/C_1
27	C_{2v}/C_{2v}	C_{2v}/C_s	C_s/C_s
28	T/T	T/T	C_3/C_s
29	C_3/C_3	C_3/C_3	C_1/C_2
30	C_{2v}/C_s	C_s/C_s	C_{3v}/C_{3v}
31	C_s/C_3	C_3/C_3	C_3/C_3
32	D_3/D_3	D_3/D_3	C_3/D_{2d}
33	C_2/C_2	C_2/C_2	C_2/C_2
34	C_s/C_s	C_s/C_s	C_2/T_d
35	C_{2v}/D_3	C_{2v}/D_3	C_{2v}/C_{2v}
36	C_s/C_s	C_s/C_1	C_{2v}/C_{2v}
37	C_2/C_2	C_2/C_2	C_1/C_{2v}
38	O_h/O_h	O_h/O_h	C_2/O_h
39	C_{5v}/C_5	C_5/C_5	D_3/D_3
40	C_s/C_s	C_s/C_s	D_2/D_3
41	C_s/C_1	C_1/C_3	D_2/C_1
42	C_s/D_2	D_2/D_2	C_2/D_4
43	C_s/C_s	C_s/C_s	C_1/D_2
44	C_1/C_s	C_s/C_s	C_1/C_s
45	C_s/C_s	C_s/C_s	C_1/C_s
46	C_{2v}/C_{2v}	C_{2v}/C_{2v}	C_1/C_3
47	C_1/C_1	C_1/C_1	C_1/C_1
48	C_s/C_s	C_s/C_s	C_1/C_1
49	C_{3v}/C_{3v}	C_{3v}/C_{3v}	C_1/C_1
50	C_s/C_s	C_s/C_s	C_1/C_1
51	C_{2v}/C_{2v}	C_{2v}/C_{2v}	C_1/C_1
52	C_{3v}/C_{3v}	C_{3v}/C_{3v}	C_{2v}/D_{5d}
53	C_{2v}/C_{2v}	C_{2v}/C_{2v}	C_{3v}/C_{5v}
54	C_{5v}/C_{5v}	C_{5v}/C_{5v}	C_1/I_h
55	I_h/I_h	I_h/I_h	C_1/C_{3v}
56	C_{3v}/C_s	C_s/C_s	C_2/C_s
57	C_s/C_s	C_1/C_s	C_1/C_1
58	C_{3v}/C_{3v}	C_{3v}/C_{3v}	C_1/C_1
59	C_{2v}/C_{3v}	C_1/C_1	C_1/C_s
60	C_s/C_s	C_s/C_s	C_s/C_s

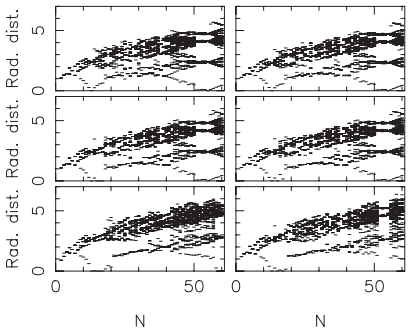

Fig. 3. The radial distance (in Å) for (from above) Ni, Cu, and Au clusters as calculated using (right) the DBF and (left) the VC potential. In each panel a horizontal line for a given value of N indicates that at least one atom has that distance to the center of the cluster.

with $\boldsymbol{R}_i$ being the position of the ith atom. Then, $d_i = |\boldsymbol{R}_i - \boldsymbol{R}_0|$ is the radial distance for the ith atom. In a graphical representation, we subsequently mark, for each value of N, those values of d_i that are found and show these as a function of N, cf. Figure 3. When only few values are found for a given N, the cluster has a high symmetry with few atomic shells. This is, e.g., found for all systems and potentials around $N = 55$, except for the Au_{55} cluster obtained with the VC potential. It is interesting to observe how this property is not concentrated to the single values of N but that it is built up over a larger or smaller range of N values.

In the figure we also see that the two potentials for Ni and Cu lead to very similar results, which is not the case for Au, once again confirming that Au is a material for which small, critical parts of the potential may lead to significantly different results. Moreover, we observe that the results for Ni and Cu resemble each other, whereas those for Au are different, with the results using the VC potential being more close to those for Ni and Cu than those obtained with the DBF potential, which, in turn, seems to indicate irregular structures of low symmetry.

4 Conclusions

In this study we have reported results of an unbiased structure optimization of Ni, Cu, and Au clusters with up to 60 atoms using two different potentials within the EAM framework. Since we have used the same unbiased structure-optimization method, our study allows for a direct comparison of the performances of the two potentials. To our knowledge, no such unbiased study has been presented before.

It was very clear that the structure of Au_N depends critically on the used potential which may be an explanation for the large scatter in the results that have been obtained theoretically for this system, as discussed in the introduction. On the other hand, the weak sensitivity of the results for Ni and Cu on the potential makes us propose that this may be a more general property for those systems, i.e., also other theoretical approaches should give results that only differ little from those presented here.

Moreover, we found that Ni and Cu clusters are very identical and that also the sequence of magic numbers for those is similar for the two systems. In contrast, once again Au clusters showed a markedly different behavior. Finally, whereas both EAM potentials gave realistic results for Ni and Cu, only the VC parameterization was considered useful for Au.

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References

1. O.D. Häberlen et al., J. Chem. Phys. **106**, 5189 (1997)
2. J. Wang et al., Phys. Rev. B **66**, 035418 (2002)
3. J. Wang et al., Chem. Phys. Lett. **380**, 716 (2003)
4. G. Bravo-Pérez et al., J. Mol. Str. (Theochem) **493**, 225 (1999)
5. H. Grönbeck, W. Andreoni, Chem. Phys. **262**, 1 (2000)
6. L. Lamare, F. Michel-Calendini, Int. J. Quant. Chem. **61**, 635 (1997)
7. H. Häkkinen, U. Landman, Phys. Rev. B **62**, 4 (2000)
8. J. Olviedo, R.E. Palmer, J. Chem. Phys. **117**, 21 (2002)
9. C. Massobrio et al., J. Chem. Phys. **109**, 16 (1998)
10. H. Åkeby et al., J. Phys. Chem. **94**, 5471 (1990)
11. P. Calaminici et al., J. Chem. Phys. **105**, 21 (1996)
12. I.L. Garzón, A. Posada-Amarillas, Phys. Rev. B **54**, 11796 (1996)
13. N.T. Wilson, R.L. Johnston, Eur. Phys. J. D **12**, 161 (2000)
14. I.L. Garzón et al., Phys. Rev. Lett. **81**, 8 (1998)
15. I.L. Garzón et al., Eur. Phys. J. D **9**, 211 (1999)
16. K. Michaelian et al., Phys. Rev. B **60**, 3 (1999)
17. S. Darby et al., J. Chem. Phys. **116**, 4 (2002)
18. J. Rogan et al., Eur. Phys. J. D **28**, 219 (2004)
19. A. Sebetci, Z.B. Güvenç, unpublished
20. M. Kabir et al., Phys. Rev. A **69**, 043203 (2004)
21. T.X. Li et al., Phys. Lett. A **267**, 403 (2000)
22. C.L. Cleveland et al., Phys. Rev. Lett. **79**, 10 (1997)
23. R.N. Barnett et al., Eur. Phys. J. D **9**, 95 (1999)
24. C.L. Cleveland et al., Z. Phys. D **40**, 503 (1997)
25. F. Baletto et al., J. Chem. Phys. **116**, 9 (2002)
26. J.P.K. Doye, D.J. Wales, New J. Chem. 733 (1998)
27. V.G. Grigoryan, M. Springborg, Phys. Chem. Chem. Phys. **3**, 5125 (2001)
28. V.G. Grigoryan, M. Springborg, Chem. Phys. Lett. **375**, 219 (2003)
29. V.G. Grigoryan, M. Springborg, Phys. Rev. B **70**, 205415 (2004)
30. H. Häkkinen, M. Moseler, O. Kostko, N. Morgner, M. Hoffmann, B.V. Issendorff, unpublished
31. M.S. Daw, M.I. Baskes, Phys. Rev. Lett. **50**, 1285 (1983)
32. M.S. Daw, M.I. Baskes, Phys. Rev. B **29**, 6443 (1984)
33. S.M. Foiles et al., Phys. Rev. B **33**, 7983 (1986)
34. A.F. Voter, S.P. Chen, in *Characterization of Defects in Materials*, edited by R.W. Siegal, J.R. Weertman, R. Sinclair, *MRS Symposia Proceedings No. 82* (Materials Research Society, Pittsburgh, 1987), p. 175
35. A. Voter, Los Alamos Unclassified Technical Report No LA-UR 93-3901, 1993
36. A.F. Voter, in *Intermetallic Compounds*, edited by J.H. Westbrook, R.L. Fleischer (John Wiley and Sons, Ltd, 1995), Vol. 1, p. 77
37. V.A. Spasov et al., J. Chem. Phys. **112**, 4 (2000)
38. M.D. Morse, Chem. Rev. **86**, 1049 (1986)