A possible packing sequence of nickel clusters: Ni$_{13}$–Ni$_{32}$

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Abstract. We have carried out computer simulations to identify and characterize the ground-state geometrical structures of some nickel clusters (Ni$_{13}$–Ni$_{55}$) using tight-binding molecular dynamics. A possible geometrical packing sequence was found for Ni$_{13}$–Ni$_{32}$. The result suggested that the geometrical structures of Ni$_{13}$–Ni$_{32}$ should tend to exhibit geometries based on the icositetrahedron but not the icosahedron.

1. Introduction

To answer the question of how the atoms are packed together in clusters is extremely difficult both experimentally and theoretically. The most commonly used experimental tools for probing the structures of supported clusters, such as transmission electron microscopy and x-ray diffraction are not applicable to small clusters. Another important experimental technique for determining metal cluster structures is the chemical probe method. Recently, experiments have been performed using chemical reactions as a probe of various structural features of metal clusters [1]–[8]. These studies often yield clues about the structures of specific clusters such as the numbers and types of binding sites. Although this approach provides very valuable information, generally it does not conclusively determine the structure of the clusters.

The experimental difficulties encountered in the characterization of small metal clusters on the one hand, and their technological importance on the other hand, stimulate the need for theoretical calculations which would predict cluster properties. There have been many calculations on nickel clusters using a variety of techniques, including: ab initio CI and valence bond approaches [9], density functional theory (DFT) [10]–[12], the embedded atom method (EAM) [13, 14], the Sutton–Chen potential [15], the effective medium theory [16], the corrected effective medium (CEM) [17]–[19] and tight-binding (TB) molecular dynamics (MD) [20] methods. For those clusters whose atoms number larger than 20, some theories only assume...
spherically symmetric nickel atoms (i.e. no directional bonding) and do not take into account possible Jahn–Teller distortions of electronically degenerate configurations, and it is known that ignoring directional bonding in the $d$ manifold in structure calculations can yield incorrect structures for some nickel clusters. Moreover, most theoretical calculations for the $\text{Ni}_n$ cluster rely on cluster geometries chosen \textit{a priori}, but not full geometric optimization by MD. To date, except for the icosahedral structures of $\text{Ni}_{13}$ and $\text{Ni}_{55}$, which have been completely determined, many divergences and doubts about the structures of nickel clusters still exist between the theoretical predictions and experiments. For example, is the growth pattern of nickel clusters (with $n < 55$) nontrivial, or based on an open icosahedral geometry, or based on the cuboctahedral geometry or another kind of geometry?

The TB approximation may be characterized as the simplest formulation of atomic interactions that incorporates the quantum mechanical nature of bonding. A particular feature that it captures is that the strength of a bond is dependent not only on the interatomic separation but also on the angles it forms with respect to the other bonds, which arises fundamentally from the spatially directed characters of $p$ and $d$ atomic orbitals. It enjoys more of the accuracy of the \textit{ab initio} simulations than empirical potentials, but is typically two to three orders of magnitude faster than \textit{ab initio} techniques.

In this paper, we present a computer study of $\text{Ni}_n$ ($n = 5$–32) based on TB MD simulations, aimed at improving our basic understanding of the nickel growth phenomena. The present computer-intensive investigation has been carried out by simulated annealing using MD based on a transferable TB potential for nickel [21].

2. Computational scheme

In the TB MD scheme model, the total energy is written as

$$E_{\text{tot}} = \sum_i \frac{p_i^2}{2m} + \sum_n \langle \psi_n | H_{\text{TB}} | \psi_n \rangle + E_{\text{rep}}.$$  

(1)

The first term is the kinetic energy of the ions, the second term is the electronic energy calculated by summing eigenvalues of all occupied electronic states from a TB Hamiltonian $H_{\text{TB}}$, and $E_{\text{rep}}$ is a repulsive potential representing the ion–ion repulsion and correcting for the double counting of the electron–electron interaction of the second term. In the present simulation, a TB Hamiltonian for Ni proposed by Luo was used. The model uses a minimal basis of $s$, $d$ orbitals to construct the TB Hamiltonian $H_{\text{TB}}$ for the electronic structure calculations, namely,

$$H_{\text{TB}} = \sum_i \sum_{\alpha=s,d} \varepsilon_{\alpha} a_{i\alpha}^{+} a_{i\alpha} + \sum_{i,j} \sum_{\alpha,\beta=s,d} h_{i\alpha,j\beta} a_{i\alpha}^{+} a_{j\beta}. $$  

(2)

The parameters in the potential were chosen by fitting first-principles local density approximation (LDA) results of total energy versus atomic volume for different nickel polytypes [22], i.e. face-centred cubic (fcc), body-centred cubic (bcc), simple hexagonal (s hex), simple cubic (s cubic) and diamond cubic (d cubic) structures, so that the potentials have good transferability in various kinds of atomic environments. Details of the potential model can be found in [21].

The problem of finding the total-energy global minimum as a function of structure is especially difficult in the multi-dimensional case, because the number of local minima increases rapidly with increasing $N$. Although the TB method is much faster than \textit{ab initio} techniques, it is still much slower than simple empirical potentials such as the EAM. In order to search for the global minimum we adopted the following procedure that included several steps:

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Table 1. Comparison of our results for the small Ni$_2$ and Ni$_{13}$ clusters with the \textit{ab initio} DFT computations \cite{23}, EAM method \cite{14} and available experimental data \cite{24}.

|                  | $\Delta E_B = E_B(13) - E_B(2)$ (eV$^{-1}$) | Bond length in Ni$_2$ (Å) | Bond length in Ni$_{13}$ (Å) |
|------------------|---------------------------------------------|---------------------------|-----------------------------|
| This work        | 1.620                                       | 2.09                      | 2.38                        |
| SIESTA           | 1.558                                       | 2.17                      | 2.41                        |
| EAM              | 1.525                                       | 2.13                      | 2.36                        |
| Experiment       | 2.20                                        |                           |                             |

Figure 1. Geometric structures of Ni$_5$–Ni$_{12}$.

(1) Each cluster’s starting configuration was achieved by placing atoms randomly in a cube and letting each atom separate from any other atoms, and the walls of the cube not too far or not too close (between 2 and 3 Å). Then the cluster was first heated to 1000 K by renormalizing the velocities at each timestep and slowly annealing to 10 K through an up to 50 000 timestep MD calculation (timestep = $1.0 \times 10^{-15}$ s).

(2) A cluster configuration with the lowest energy of a cluster with $N$ atoms was found by performing step 1 for 30 randomly chosen starting geometries.

(3) The cluster with the lowest minimum is reheated to 1000 K and slowly cooled to 10 K, once again using up to 50 000 timesteps, and the new optimized coordinates and energy are found. Of the two minima, old and new, the lowest is selected. If the lowest is old, the search for the global minimum is over. If the lowest is new, then repeat steps 1 and 2.

With this strategy we may have obtained optimized values for the cluster energies which either coincide or lie close to the global minima.

3. Results and discussion

To demonstrate that our TB potential parameters are appropriate for the cluster calculations, we first compare our results with \textit{ab initio} MD simulations obtained with the self-consistent DFT program SIESTA \cite{23}, EAM \cite{14} and available experimental information for the Ni$_2$ molecule \cite{24} presented in table 1. We observe a good agreement for the listed values. Furthermore, we describe the structures of Ni$_5$–Ni$_{12}$, and make some comparisons with results.
of other researchers to show the transferability of the potential parameters. Then we discuss the geometries of Ni_{13}–Ni_{32} in detail. The structures we obtained for Ni_{5}–Ni_{12} are displayed in figure 1. Ni_{5} is a non-planar structure composed of three triangles which looks something like a butterfly. The structure of Ni_{6} is placed one atom above the central triangle of Ni_{5}, and the atom pulls two other more distant atoms closer so that a double triangular pyramid is formed. For Ni_{5}, experimental results [1] suggested that Ni_{5} should have a trigonal bipyramid structure. Stave and DePristo (SD) [10] predicted only one stable structure, the trigonal bipyramid, by using CEM theory. However, Nygren et al [9] determined a completely different stable configuration (a planar triangular array) using an ab initio method for Ni_{5}, which is in agreement with our result. For Ni_{6}, the experimental results [1] implied that the octahedron should be the most likely structure for Ni_{6}, which is the same as the result given by SD. Nygren et al [9] predicted a pentagonal pyramid for Ni_{6}, which did not agree with the experimental result. Michaelian et al [25] predicted three lowest energy isomers with an n-body Gupta potential. The second isomer of the three lowest energy isomers is completely in agreement with our result. For Ni_{7}, the chemical reaction experimental result of Parks et al [1] suggested that Ni_{7}N_{2} should have the capped octahedron structure. Whether the bare cluster has the same structure cannot be stated with certainty. Experimental results from the uptake pattern for ammonia [7] on this cluster implied that the pentagonal bipyramid should be the most likely structure. Our calculations also found these two structures, a capped octahedron and a pentagonal bipyramid. The capped octahedron is 0.42 eV lower in energy than the pentagonal bipyramid. This is identical to the structure inferred from N_{2} uptake experiments [1]. Recently, two additional ab initio calculations and a semi-empirical potential calculation have been carried out on Ni_{7} by Nayak et al [26] and Curotto et al [27], respectively. They both report two structures, a capped octahedron and a pentagonal bipyramid. The capped octahedron is reported by these authors to be 0.35 and 0.24 eV lower in energy than the pentagonal bipyramid, respectively. For Ni_{8}, Parks et al [1, 7] came to the conclusion that Ni_{8} has a bisdisphenoid structure (a D_{2d} dodecahedron). The eight-atom dodecahedron has four equivalent four-coordinate atoms and four equivalent five-coordinate atoms. Their evidence for a bisdisphenoid Ni_{8} came from the uptake pattern for ammonia on this cluster. Ammonia uptake experiments [7] with Ni_{8} showed the average number of adsorbed ammonia molecules $m$ versus the partial pressure of ammonia in the cluster source and flow-tube reactor (FTR) has plateau at $m = 4$ and 8, which implied that it possibly should have a bisdisphenoid structure. SD also obtained the bisdisphenoid for Ni_{8}, but our calculation predicts two isomers for Ni_{8}, a distorted bicapped trigonal prism and a distorted bicapped octahedron. The bicapped trigonal prism is 0.48 eV lower in energy than the distorted bicapped octahedron. These results also agree with the results of Nayak et al [26] and Curotto et al. It is noted that the structure of the bicapped octahedron may also be consistent with the ammonia uptake experiments. Since the eight-atom bicapped octahedron has two equivalent three-coordinate atoms and six five-coordinate atoms, each three-coordinate atom may first bind two ammonia molecules so that a plateau appears at $m = 4$, as the pressure increases, each atom could only bind one ammonia molecule so that another plateau appears at $m = 8$. Ni_{9} is the tricapped trigonal prism. For Ni_{10} and Ni_{11}, the results of our calculation suggested that they should be a capped square antiprism and a capped trigonal prism, respectively. The geometry of Ni_{10} has D_{4d} symmetry. These two geometric packing structures also agree with the predictions of Curotto et al. The result for Ni_{12} shows a icosahedral structure minus one atom, which agrees with the result of Michaelian et al [25]. It is clear that our potential parameters are appropriate for the nickel cluster system. Moreover, we find that it is clear that the growth pattern is nontrivial for $N < 13$. 

New Journal of Physics 4 (2002) 10.1–10.8 (http://www.njp.org/)
Figure 2. Geometric packing sequence of nickel clusters with a number of atoms ranging from 13 to 32.

Although some local minima have been observed for every cluster, we only show the isomer with lowest energy here. Figure 2 displays the geometric structure results for Ni$_{13}$–Ni$_{31}$. A clear growth sequence for Ni$_{13}$–Ni$_{31}$ can be found from the figure. Ni$_{13}$ was a first cluster with core atom, its structure is an icosahedron, which has one core atom. This result agrees with many experiments and theoretical calculations [2, 7, 10, 28]. The addition of an atom makes one planar pentagon of the icosahedron the first hexagonal atom arrangement (hexagonal ring), which is the structure of Ni$_{14}$. The addition of another atom makes the opposite planar pentagon of the icosahedron form the second hexagonal ring, which formed an icositetrahedron, it is just the structure of Ni$_{15}$. Although the structures of Ni$_{16}$–Ni$_{18}$ are somewhat distorted from the symmetry of the icositetrahedron, they still hold the two hexagonal rings, only change their bottom atoms from one of the Ni$_{15}$ to two and further to three and four, respectively. Ni$_{19}$ is formed by placing one atom underneath the bottom square of Ni$_{18}$. Although the addition of this atom makes the two hexagonal rings bend prominently in the same direction, it actually results in the structure of Ni$_{19}$ being high-symmetry D$_{4d}$. It should be noted that Ni$_{19}$ has only one core atom. This does not agree with the speculation of some other researchers [2, 7]. They suggested that Ni$_{19}$ should have the structure of a double icosahedron, which has two core atoms.

Figure 2(j) clearly suggests that the structure of Ni$_{22}$ should be a perfect double-interpenetrating icositetrahedron, which has three parallel hexagonal rings. Ni$_{21}$ is formed...
by removing an atom from the bottom hexagonal ring of Ni$_{22}$, so that the bottom hexagonal ring turns into a pentagonal ring. Ni$_{23}$ was formed by merely adding one atom to the bottom of Ni$_{22}$, so that one bottom apex atom turns into two apex atoms. Ni$_{24}$ was formed by the addition of one atom to the top of Ni$_{23}$, so that one top apex atom turns into two apex atoms. Similarly, Ni$_{25}$ and Ni$_{26}$ are formed by further placement of one atom at the bottom of Ni$_{24}$ and Ni$_{25}$, respectively. The structure of Ni$_{27}$ is seriously distorted from Ni$_{26}$, but it can still be thought of as the addition of an atom to the top of Ni$_{26}$, so that the two top apex atoms turn into three top apex atoms, and at the same time it seriously distorted the waist part of the structure. Ni$_{28}$ is constructed by adding four atoms on the adjacent top four triangles of Ni$_{23}$, respectively, and then placing an atom above the four atoms. It has C$_{2v}$ symmetry. Ni$_{29}$ is formed by further addition of one atom to the top of Ni$_{28}$. The atom makes the top square atom arrangement turn into a pentagonal ring. Furthermore, adding one atom will make the top pentagonal ring of Ni$_{29}$ turn into a hexagonal ring, and this is just about the structure of Ni$_{30}$. This structure can also be thought of as a 22-atom double-interpenetrating icositetrahedron (Ni$_{22}$) interpenetrating a 23-atom structure based on the icositetrahedral Ni$_{23}$. Ni$_{31}$ can be thought of as two interpenetrating Ni$_{23}$ clusters. Although the geometry of Ni$_{32}$ differs greatly from the Ni$_{31}$ structure, it still includes a whole icositetrahedron in its geometry, and its packing pattern is still based on double-interpenetrating icositetrahedra, only with ten atoms packing out one side of the double-interpenetrating icositetrahedron. According to our further calculations for larger clusters, as the number of atoms increases, the packing geometries of larger clusters become much more complex and show us structural multiplicity for Ni$_{33}$–Ni$_{54}$ so that we cannot describe them clearly by a certain packing sequence. Details of those results for Ni$_{33}$–Ni$_{55}$ have been published in [29]. However, the structure of Ni$_{55}$ we obtained is distorted icosahedral, which agrees completely with the prediction of some experiments and theories [4, 7, 19].

A central issue in cluster physics is to identify particularly stable sizes. Figure 3 shows the second finite difference of the total energy, i.e. the stability function

$$ S(N) = E_{tot}(N + 1) + E_{tot}(N - 1) - 2E_{tot}(N) $$

as a function of cluster size. The peaks shown in figure 3 correspond to the most stable structures (often termed magic clusters), the minima, to the most unstable. The following magic numbers

\[ \text{Ni}_{55} \]
are observed: 13, 17, 19, 21, 23, 29, 31, 33, 35, 38, 40, 43, 45, 47, 50, 55. The corresponding sizes for the most unstable clusters are: 12, 14, 20, 22, 26, 30, 32, 34, 37, 39, 42, 44, 49, 53. In [14], the corresponding peaks in the $S(N)$ appear at $N = 13, 19, 23, 27, 29, 43, 46, 49, 55$ and the corresponding minima are: 12, 14, 18, 22, 26, 30, 32, 34, 37, 39, 42, 44, 49, 51. Out of all the peaks, six peaks out of nine peaks in [14] and seven peaks out of 12 peaks in [15] emerge in our calculation. But only four peaks are the same in [14] and [15]. Peaks at $N = 13, 19, 55$ emerge in all calculations. Among all minima, six minima of 11 in [14] and [15] emerge in our calculation. However, only four minima are the same in [14] and [15]. The minima of $S(N)$ at $N = 12, 14$ emerge in all calculations. It is clear that further calculations with more accurate methods are needed to identify magic clusters.

4. Conclusions

In summary, simulations of transferable TB MD with an annealing technique have been used to characterize and predict the growth of nickel clusters. We have demonstrated that our TB potential parameters are appropriate for the nickel cluster system. Ground state geometric structures for every cluster with atoms numbering five and 32 have been presented and we found that there is definitely a growth sequence, which based on the icositetrahedron, occurs for Ni$_{13}$–Ni$_{32}$.

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References

[1] Parks E K, Zhu L, Ho J and Riley S J 1994 J. Chem. Phys. 100 7206
[2] Parks E K, Zhu L, Ho J and Riley S J 1995 J. Chem. Phys. 102 7377
[3] Ho J, Zhu L, Parks E K and Riley S J 1993 J. Chem. Phys. 99 1409
[4] Parks E K and Riley S J 1995 Z. Phys. D 33 59
[5] Parks E K, Nieman G C, Kerns K P and Riley S J 1997 J. Chem. Phys. 107 1861
[6] Ho J, Zhu L, Parks E K and Riley S J 1993 Z. Phys. D 26 331
[7] Parks E K, Winter B J, Klots T D and Riley S J 1991 J. Chem. Phys. 94 1882
[8] Parks E K, Winter B J, Klots T D and Riley S J 1992 J. Chem. Phys. 96 8257
[9] Nygren M A, Siegbahn P E M, Wahlgren U and Akeby H 1992 J. Phys. Chem. 96 3633
[10] Pastor G M, Dorantes-Davila J and Bennemann K H 1989 Phys. Rev. B 40 7642
[11] Stave M S and DePristo A E 1992 J. Chem. Phys. 97 3386
[12] Rösch N, Ackermann L and Pacchioni G 1992 Chem. Phys. Lett. 199 275
[13] Russier V, Salahub D R and Mijoule C 1990 Phys. Rev. B 42 5046
[14] Pacchioni G, Chung S, Krueger S and Rösch N 1994 Chem. Phys. 184 125
[15] Daw M S, Foiles S M and Baskes M I 1993 Mater. Sci. Rep. 9 251
[16] Norskov J K 1991 Prog. Surf. Sci. 38 103
  Stoltze P 1994 J. Phys.: Condens. Matter 6 9495
  Christensen A, Stoltze P and Norskov J K 1995 J. Phys.: Condens. Matter 7 1047

New Journal of Physics 4 (2002) 10.1–10.8 (http://www.njp.org/)
[17] Kress J D and DePristo A E 1987 *J. Chem. Phys.* **87** 4700
[18] Stave M S and DePristo A E 1992 *J. Chem. Phys.* **97** 3386
[19] Wetzel T L and DePristo A E 1996 *J. Chem. Phys.* **105** 572
[20] Lathiotakis N N, Andrioties A N, Menon M and Connolly J 1995 *Europhys. Lett.* **29** 135
[21] Luo C 2000 *Modelling Simul. Mater. Sci. Eng.* **8** 95
    Luo C 1998 *Modelling Simul. Mater. Sci. Eng.* **6** 603
[22] Paxton A T, Methfessel M and Polatoglou H M 1990 *Phys. Rev.* B **41** 8127
[23] Calleja M, Rey C, Alemany M M G, Gallego L J, Ordegon P, Sanchez-Portal D, Artacho E and Soler J M 1999 *Phys. Rev.* B **60** 2020
[24] Noell J O, Newton M D, Hay P J, Martin R L and Bobrowicz F W 1980 *J. Chem. Phys.* **73** 2360
[25] Michaelian K, Rendón N and Garzón I L 1999 *Phys. Rev.* B **60** 2000
[26] Nayak S K, Reddy B, Rao B K, Khanna S N and Jean P 1996 *Chem. Phys. Lett.* **253** 390
[27] Curotto E, Matto A and Freeman D L 1998 *J. Chem. Phys.* **108** 729
[28] Kerns K P, Parks E K, and Riley S J 2000 *J. Chem. Phys.* **112** 3394
[29] Luo C 2002 *Modelling Simul. Mater. Sci. Eng.* **10** 13