Theoretical Study of the Structures and Stabilities of Iron Clusters†

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Abstract

An empirical many-body potential energy function, derived previously by fitting data for two allotropes of iron (bcc and fcc), has been applied to the study of the structures and relative stabilities of iron clusters with up to 671 atoms. For small clusters, growth is predicted to occur *via* the fusion of tetrahedral units, leading eventually to icosahedral clusters. A subset of larger clusters, with high symmetries and shell structures (so called Geometric Shell Magic Number Clusters) was studied and the stability order icosahedral > rhombic dodecahedral (bcc) > decahedral > cuboctahedral (fcc) established in the nuclearity range studied, though crossover of stability between icosahedral and (bulk-like) bcc structures is predicted to occur at around 2000 atoms.

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† Dedicated to Professor John N. Murrell.

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1. Introduction

There is considerable experimental interest in the study of gas phase metal clusters, for a number of reasons.[1] Firstly, they constitute intermediates between molecules, with clearly defined energy states (electronic, vibrational *etc.*) and condensed matter where these states form continua or bands. It is clearly important to know how bulk properties develop as a function of cluster size.[2] The high ratio of surface atoms to bulk atoms (where the term "surface" refers to any atom having fewer neighbours than it would have in the bulk lattice) also means that there are many points in common between the chemistry and physics of clusters and of solid surfaces. Clusters are also of interest in their own right, since for small clusters there is the possibility of finite size effects leading to electronic, magnetic or other properties which are quite different from those of molecules or condensed matter. There has also been a considerable research effort into understanding the geometries, stabilities and reactivities of gas phase bare metal clusters from a theoretical view point.[3]

For iron, there have been a number of experimental studies of the generation, reactivity and magnetism of gas phase clusters with up to several hundreds of atoms.[4,5,6,7,8,9] Electronic structure calculations have also been performed on iron clusters,[10,11,12,13] using *ab initio* methods for small clusters (up to ten atoms) over a limited range of configuration space and more approximate Hamiltonians for larger clusters (tens of atoms). However, for larger clusters, with hundreds or thousands of atoms, even approximate electronic structure calculations become prohibitive in terms of time and expense. Thus, in order to simulate the properties of large iron clusters, there is a need for accurately parameterised empirical potential energy functions (PEFs) which are atomistic in nature (*i.e.* they depend only on the atomic positions and do not include the electrons explicitly) and which can be computed rapidly.

In this study, we apply an empirical atomistic potential, consisting of 2-body and 3-body terms, which has been fitted to bulk properties of iron, to investigate the relative stabilities of iron clusters of between 2 and 671 atoms. In this way, we wish to establish the suitability of such a potential for accurately describing properties of both large and small clusters. The initial motivation for this work was to find low energy geometries for iron clusters with up to several hundreds of atoms, to serve as model structures in the simulation of cluster magnetism.[14,15]

Results for clusters in the range 2-20 atoms can be compared with *ab initio* results and used to establish the general suitability of the empirical potential for studying the structures, stabilities and dynamics of iron clusters, while the study of the larger clusters facilitate the comparison of different structure types and in particular allow one to address the problem of the approach of cluster structure and binding energy to those of the solid as the cluster nuclearity increases.

The PEF that we have adopted is described in Section 2(a), and the computational methods employed in this study are summarised in Section 2(b). Section 3 presents a review of "Magic Number" cluster nuclearities arising due to the completion of geometric shells of atoms. The results of geometry optimisations/energy minimisations using our PEF are presented in Section 4(a-c): for small iron clusters (Fe_2-Fe_{20}); for large Magic Number Clusters (MNCs) based on pseudo-spherical icosahedral, cuboctahedral (fcc), decahedral and rhombic dodecahedral (bcc) geometries; and for fcc-derived MNCs with non-spherical topologies. The results of our calculations are then compared, in Section 5, with experimental data and with the results of previous electronic structure and PEF calculations on clusters of iron and other transition metals.

2. Computational Procedure

(a) The potential energy function for iron

In a number of recent papers,[16] Murrell and co-workers have introduced a potential energy function (the so-called Murrell-Mottram [MM][16a] potential), consisting of 2-body and 3-body terms, for modelling atomic solids, surfaces and clusters. This potential, which is obtained by fitting lattice dynamical data pertaining to one or more allotropes of a given element, has the following form for the 2-body potential between atoms i and j and the 3-body potential involving atoms i, j and k:

$$V_{ij}^{(2)} = -D(1+a_2\rho_{ij})\exp(-a_2\rho_{ij}) \tag{1}$$

$$V_{ijk}^{(3)}=D\times P(Q_1,Q_2,Q_3)\exp(-a_3Q_1) \tag{2}$$

where

$$\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix} = \begin{pmatrix} \sqrt{1/3} & \sqrt{1/3} & \sqrt{1/3} \\ 0 & \sqrt{1/2} & -\sqrt{1/2} \\ \sqrt{2/3} & -\sqrt{1/6} & -\sqrt{1/6} \end{pmatrix} \begin{pmatrix} \rho_{ij} \\ \rho_{ik} \\ \rho_{jk} \end{pmatrix} \tag{3}$$

and

$$\rho_{ij} = (r_{ij} - r_e)/r_e \tag{4}$$

with r_{ij} being the distance between atoms i and j. a_2 and a_3 are the range exponents for the 2- and 3-body potentials respectively and D and r_e are scaling factors which ensure that the lattice energy and lattice spacing of the ground state structure are reproduced exactly. The function P is a polynomial (which is totally symmetric with respect to interchange of atoms) in the symmetry coordinates Q_i. At the quartic level this polynomial takes the form:

$$\begin{aligned} P(Q_1,Q_2,Q_3) = {} & c_0 + c_1Q_1 + c_2Q_1^2 + c_3(Q_2^2+Q_3^2) + c_4Q_1^3 \\ & + c_5Q_1(Q_2^2+Q_3^2) + c_6(Q_3^3-3Q_3Q_2^2) + c_7Q_1^4 \\ & + c_8Q_1^2(Q_2^2+Q_3^2) + c_9(Q_2^2+Q_3^2)^2 + c_{10}Q_1(Q_3^3-3Q_3Q_2^2) \end{aligned} \tag{5}$$

The application of these potentials to a variety of metallic and non-metallic elemental solids[17] and clusters[18] has been described in the literature. Gao, Johnston and Murrell (GJM) have recently derived a (MM) potential which gives a good description of the lattice dynamics and relative energies of two allotropes of iron; low temperature (bcc) α-Fe and high temperature (fcc) γ-Fe.[19] The parameters defining this potential are listed in Table 1. The suitability of such a potential, derived by fitting bulk properties, for the description of clusters cannot be assumed and can only be established after careful comparison with both experimental and *ab initio* results.

(b) Methodology

For clusters of up to 20 atoms the program CLUSPRO was used to optimise cluster geometries. Starting geometries were either fragments of cubic (diamond, simple cubic, bcc or fcc) solids or icosahedral fragments, or were generated randomly. CLUSPRO optimises cluster geometries using NAG[20] routines E04KAF (quasi-Newton steepest descent algorithm using analytic first derivatives), E04LAF (modified-Newton steepest descent algorithm using analytic first and second derivatives) and E04DGF (quasi-Newton conjugate gradient algorithm using analytic first derivatives).[21] Since both steepest descent and conjugate gradient methods can converge to saddle points as well as minima, analytic first and second derivatives of the potential were also used to calculate cluster vibrational frequencies; the order of a stationary point being equal to the number of imaginary frequencies.

For the series of "magic number" fcc, icosahedral (ico), decahedral (dec) and bcc clusters, with up to 671 atoms, energy minimisation was performed using a program, developed by Wales and co-workers,[22] which employs a conjugate gradient algorithm[23] and analytic first and second derivatives of the potential (the latter for checking the order of stationary points). The reader is directed to the detailed analysis, by Uppenbrink and Wales (U&W), of the relative stabilities of high nuclearity shell clusters with cuboctahedral, icosahedral and decahedral morphologies as a function of cluster size and for several different types of potential (2-body, 2-plus-3-body and many-body).[24]

3. Geometric Shells and Magic Number Clusters

For small clusters of simple metals, such as the alkali metals, mass spectroscopic studies have indicated the presence of preferred nuclearities or *"magic numbers"* corresponding to particularly intense peaks.[25] These experiments led to the development of the (spherical) *jellium* model, wherein the actual cluster geometry (*i.e.* nuclear coordinates) are unknown and unimportant (perhaps because the clusters are molten or rapidly fluxional) and the cluster valence electrons are assumed to move in a spherically average central potential.[26] The jellium model therefore explains cluster magic numbers in terms of the filling of cluster **electronic shells**, which are analogous to the electronic shells in atoms. For somewhat larger nuclearities (N ~ 100-1500) there are periodic oscillations in mass spectral peak intensities whish have been attributed to the bunching together of electronic shells into supershells.[27]

The observation of long period oscillations in the intenstities of peaks in the mass spectra of very large metal clusters (with up to 10^5 atoms) has lead to the conclusion that such clusters grow *via* the formation of 3-dimensional concentric **geometric shells** of atoms and that for these nuclearities it is the filling of geometric rather than electronic shells that imparts extra cluster stability.[28] That electronic effects are relatively unimportant for high nuclearity clusters (*i.e.* there is no electronic state specificity) is presumably because the electronic states are so close together that they form a quasi-continuum (as in a bulk metal) with no great gain or loss in stability being associated with electronic shell filling.

For transition metals there is no clear evidence that the jellium model holds, even for low nuclearities. It is interesting to postulate why this should be so. It may be because the valence d electrons of a transition metal element are more tightly bound than the valence s and p electrons of simple metals. Late transition metals such as iron, have higher effective nuclear charges and thus tend to have greater localisation of electron density than in the nearly-free electron simple metals. An alternative explanation is that d-orbitals impart angularity into bonding which cannot be reproduced in a central field potential such as in the jellium model. If this is the reason, then we would hope that a model which introduces explicit angular-dependent many-body forces (as in the MM model that we have adopted) will fare better at explaining cluster structure preferences. Another point worth considering is that transition metals have higher densities of electronic states than simple metals, due to the smaller dispersion of the more tightly bound d-bands and the greater orbital degeneracy. Thus the nuclearity at which the cluster electronic states form a quasi-continuum would be expected to be lower for transition metals than for s-p metals.

While there are a variety of structures which may be postulated for geometric shell clusters, in previous studies attention has mainly been focussed on close-packed and pseudo-close-packed arrangements based on: the centred cuboctahedron ("fcc", as it is a fragment of the bulk face centred cubic structure); the centred icosahedron (or "ico"); and the centred bicapped pentagonal prism (which is commonly referred to as a truncated decahedron: "dec"). These structures can be said to have pseudo-spherical topologies. In this Section we will consider these structures together with pseudo-spherical geometric shell clusters, based on the centred rhombic dodecahedron, which are fragments of the body centred cubic lattice (*i.e.* the ground state structure of bulk iron) and which we shall label as "bcc". It should be noted that such clusters have been discussed by Martin *et al.*[28] and that there has been a detailed study of rhombic dodecahedral clusters, of Ta, Mo and W (which also have bulk bcc structures) by Marville and Andreoni,[29] using a Finnis-Sinclair many-body empirical potential.[30] The basic ico, dec, fcc and bcc polyhedra are shown in Figure 1.

In this work a *polyhedral shell* (with shell index S) is defined as a *v*-vertex polyhedron of degree S, which has (S+1) atoms (including vertex atoms) along each polyhedral edge.[31] The central atom therefore constitutes the zeroth shell and all shells S>0 have the same topology as the parent polyhedron of degree one (*i.e.* S=1). It has been shown by several groups[32] that for S>0 the number of atom, n(S), in a given shell S is given by:

$$n(S) = (v-2)S^2 + 2 \qquad (6)$$

Following Martin *et al.* the geometric "magic number" (*i.e.* total number of atoms N(T)) for a cluster consisting of T complete polyhedral atomic shells plus a central atom is obtained by summing over shells S = 0→T:

$$N(T) = \sum_S n(S) + 1 = \{2(v-2)T^3 + 3(v-2)T^2 + (v+10)T + 6\}/6 \qquad (7)$$

Let us consider the magic numbers corresponding to complete polyhedral shells and sums over complete shells for the four types of polyhedra shown in Figure 1. Considering first of all the ico, dec and fcc clusters: ico clusters are based on the 12 vertex icosahedron, which has 20 triangular faces (Figure 1a); dec clusters are based on the 12 vertex bicapped pentagonal prism, which has 10 triangular and 5 square faces (Figure 1b); and fcc clusters are based on the 12 vertex cuboctahedron, which has 8 triangular and 6 square faces (Figure 1c). For each of these families of clusters *v*=12 and the number of atoms per shell (Equation 6) is:

$$n(S) = 10S^2 + 2 \qquad (8)$$

and the total number of atoms, for T shells (Equation 7), is:

$$N(T) = \{20T^3 + 30T^2 + 22T + 6\}/6 \tag{9}$$

Values of n(S) and N(T) for cuboctahedral (fcc), icosahedral (the Mackay icosahedra)[33] and decahedral (truncated Bagley decahedra)[34] clusters with up to 5 shells are listed in Table 2 and the outermost shells of atoms for the largest clusters (S=5; N=561) are shown in Figure 2a-2c.

Bcc clusters are based on the 14 vertex rhombic dodecahedron, which has 12 rhombic faces (Figure 1d). For v = 14, Equation 6 becomes:

$$n(S) = 12S^2 + 2 \tag{10}$$

and Equation 7 becomes:

$$N(T) = 4T^3 + 6T^2 + 4T + 1 \tag{11}$$

Values of the magic numbers n(S) and N(T) for bcc clusters with up to 5 shells are listed in Table 2 (see Refs. 32c,d for more comprehensive tables of magic numbers for a variety of shell cluster morphologies) and the outermost shell of atoms for S=5 (N=671) is shown in Figure 2d.

4. Results of Energy Minimisation Calculations on Iron Clusters

(a) Small Clusters Fe_n (n=2-20)

Within our model, the binding energy (per atom) of a cluster of N atoms is given by the following expression:

$$E_b = -\left(\sum_i \sum_{j>i} V_{ij}^{(2)} + \sum_i \sum_{j>i} \sum_{k>j} V_{ijk}^{(3)} \right) / N \tag{12}$$

Binding energies of the most stable geometries obtained for clusters Fe_2-Fe_{20}, using the GJM potential, are listed in Table 3 and the cluster geometries are reproduced in Figure 3. As in our previous studies of metal clusters,[17a-d] the GJM potential gives rise to dense cluster structures based on polytetrahedral fusion and eventually icosahedral growth in which the pentagonal bipyramid Fe_7 (**7**), centred-icosahedron Fe_{13} (**13**) and double-icosahedron Fe_{19} (**19**) are particularly stable, as can be seen from the plot of binding energy *vs.* cluster nuclearity shown in Figure 4. The convergence of cluster binding energy with size, to the bulk (bcc) cohesive energy of iron (4.28 eV)[35] is slow, with the binding energy of the most stable isomer of Fe_{20} being only 59% of the bulk value.

(b) Magic number (geometric shell) clusters

The MNCs were all found to relax radially, thereby maintaining their original point group symmetries: O_h for fcc and bcc clusters; I_h for icosahedral clusters; and D_{5h} for decahedral clusters. The binding energies (per atom) of the radially relaxed MNCs are listed in Table 4 and plotted against cluster nuclearity in Figure 5. Table 4 and Figure 5 show that, in the range we have studied the stability order is ico>bcc>dec>fcc but that the difference in binding energy decreases with increasing cluster size. It is interesting to note that the bcc clusters are only slightly less stable than the icosahedral structures. The binding energy calculated for the bcc-671 cluster is approximately 87% of the bulk cohesive energy of bcc iron (4.28 eV).

The stability order of the shell clusters based on 12-vertex polyhedra is ico>dec>fcc, as far as N = 561 atoms. This stability order is the same as that obtained by U&W using pairwise Lennard-Jones (LJ) and many-body Sutton-Chen (SC) potentials[36] to model clusters of fcc transition metal elements.[24] The same ordering was also found for 2-plus-3-body Lennard-Jones+Axilrod-Teller (LJ+AT) potentials, provided that the AT term was relatively small.[24] This ordering has been attributed to the greater average coordination number of atoms in the ico and dec clusters (see Table 5) compared with fcc. In Table 5 we list the average coordination numbers (N_1) for ico, dec and fcc. The ico and fcc values are taken from the table of Benfield[32c] and those for the lower symmetry dec clusters were evaluated numerically. For the ico clusters there are two distinct distances which have been grouped together as nearest neighbour for the purposes of evaluating coordination numbers, these are the inter-shell (radial) and intra-shell (tangential) bonds which differ in length by 5%. Similarly for dec clusters there are a number of distinct lengths which have been grouped together.

Although the bulk bcc lattice is not close packed, the bcc structure has 6 second nearest neighbours at a distance (R_2) which is only $2/\sqrt{3} \approx 1.15$ times the nearest neighbour distance (R_1). The second neighbour distance in bcc is much shorter than that in the fcc lattice ($R_2 = \sqrt{2} \times R_1$) and means that in the infinite bcc structure each atom has 14 atoms within a radius of $1.2R_1$. Table 5 lists the average number of nearest (N_1) and second nearest neighbours (N_2) for rhombic dodecahedral bcc shell clusters, calculated using Benfield's analytical formulae for rhombic dodecahedral clusters,[32d] as well as the sum N_1+N_2 (*i.e.* the average effective coordination number, which is 14 for bulk bcc). The geometry optimisations which we have performed on bcc clusters have shown that cluster shell relaxation leads to a decrease in the difference between R_1 and R_2 so that the average effective coordination number N_1+N_2 becomes a better measure for finite clusters than in the bulk (where no such relaxation can take place and R_2/R_1 is fixed by the symmetry of the lattice).

Comparing structures of the same "bulk" connectivity, the average coordination numbers can be understood in terms of the numbers and types of faces which the clusters possess. For example, ico clusters expose only 20 close-packed faces (which are topologically equivalent to the {111} surfaces of bulk fcc metals), dec clusters expose 10

{111} and 5 {100} (non-close-packed, therefore less stable) faces and fcc clusters have 8 {111} and 6 {100} faces. Thus, the stability order reflects the possession of a greater percentage of faces with lower surface energies.[37] As the clusters get larger they get closer in energy and eventually the stability order will cross over (*vide infra*). This reflects the smaller relative number of surface atoms (and therefore the closer value of average coordination number) and the increasing elastic strain in the non-close-packed ico and dec structures, due to packing frustration,[38] with increasing cluster size. It has been found that the rhombic dodecahedral clusters are found to be the most stable of all clusters based on the bcc lattice, because they expose 12 faces which are bcc {110}-type surfaces. The pseudo-close-packed {110} surface has the lowest surface energy for bcc metals.[39]

Northby *et al.* have shown that for multi-shell polyhedral LJ clusters (with pseudo-spherical topologies) of N atoms, the total potential energy of the cluster (V_{tot}) can be accurately written as a power series in $N^{1/3}$ as follows:[40]

$$-V_{tot} = \mathbf{a}N + \mathbf{b}N^{2/3} + \mathbf{c}N^{1/3} + \mathbf{d} \tag{13}$$

In Equation 13, **a**, **b**, **c** and **d** are constants: **a** represents the bulk or volume contribution to the cluster potential energy (cluster volume $V_c \propto N \propto R_c^3$, where R_c is the radius of the cluster); **b** represents the surface or area contribution (cluster surface area $A_c \propto R_c^2 \propto N^{2/3}$); **c** is the edge or length contribution (cluster edge length $L_c \propto R_c \propto N^{1/3}$); and **d** is the vertex contribution. If the cluster were truly spherical (as in the liquid or spherical droplet model)[41] there would be no edge or vertex atoms and terms **c** and **d** would disappear. Thus, it is apparent that constants **c** and **d** represent corrections to the liquid droplet model due to finite clusters actually being polyhedral (*i.e.* facetted). A similar expression (without the constant term **d**) was introduced by Tolman to determine the surface energies of finite particles.[42] It should be noted that we have multiplied Northby's potential energy by -1 in order to give it the same sign as the binding energy (E_b; a positive quantity) which we will ultimately be fitting. Of course this means that our values for the coefficients **a**-**d** will have the opposite signs to those of other authors.

If we divide both sides of Equation 13 by the number of atoms N, we obtain the more usual form:

$$-V_{tot} / N = \mathbf{a} + \mathbf{b}N^{-1/3} + \mathbf{c}N^{-2/3} + \mathbf{d}N^{-1} \quad (14)$$

and since, by definition (Equation 6) the cluster binding energy (per atom) $E_b = -(V_{tot} / N)$, plotting the calculated binding energies of the ico, dec, fcc and bcc shell clusters against $N^{-1/3}$, as in Figure 6, and fitting the resulting curves to Equation 14, enables us to find the polynomial coefficients (**a**-**d**) for each series of clusters.[43] The fitted coefficients are listed in Table 6, along with the approximate crossover nuclearities calculated using these coefficients.

In the bulk limit (as $N^{-1/3}$ tends to 0) the cluster binding energy E_b (= **a** for $N^{-1/3}=0$) should tend to the bulk cohesive energy (E_{coh}). From Table 6 we can see that there is very good agreement between the values of **a** for bcc and fcc clusters and the bulk cohesive energies: E_{coh}(bcc) = 4.28 eV (**a**-E_{coh} = +0.09%); E_{coh}(fcc) = 4.26 eV (**a**-E_{coh} = -0.12%). The ico and dec clusters cannot form periodically repeating 3-dimensional bulk (*i.e.* crystalline) structures but the extrapolated ($N^{-1/3}\rightarrow 0$) binding energies (**a**) for ico and dec are both less than the crystalline bcc and fcc structures; the stability order being ico≈dec<fcc<bcc, as would be expected for iron, for which the bcc structure (α-Fe) is stable at low temperatures and pressures and which converts to the fcc allotrope (γ-Fe) at around 1200 K.[44] Thus the relative values of the **a** coefficients reflect the inherent differences in stability of the bulk (or pseudo-bulk) phases and the fact that **a**(bcc)>**a**(fcc) confirms the preference of the GJM iron potential for bcc over fcc.[19]

The negative sign of **b** confirms that it is the existence of surfaces that lowers the average cluster binding energy of finite clusters relative to the bulk, though this reduction becomes less important as the clusters become larger and the proportion of surface atoms decreases (*i.e.* $N^{-1/3}$ becomes smaller). The magnitude of the **b** values varies as: bcc≈fcc>dec>ico, reflecting the surface stability order discussed above. In particular, the closeness of the **b** values for fcc and bcc clusters confirms the stability of the pseudo-close packed {110} surface of the bcc structure.

The fitted **c** values are also negative, indicating that facetted clusters (with approximately planar faces and hence with sharp edges) are inherently less stable than spherical drops for finite nuclearities, though the importance of this term will drop off very quickly as $N^{-2/3}$ becomes very small rapidly as N becomes large. It is impossible to say anything about the order of the **c** values for the various cluster morphologies because, with the exception of the dec clusters, the uncertainties in **c** are of the order of 8-12%. In addition, the values of **b**, **c** and **d** are intimately linked, since a vertex atom is also, by definition, an edge atom, and edge atoms are also surface atoms. Thus, the positive values of **d** in Table 6 should not be interpreted as meaning that the relatively exposed vertex atoms stabilise the cluster. Also, since the term **d**/N becomes negligable at very large N, the value of **d** obtained from the fitting procedure cannot be viewed as meaningful.

Table 6 also lists the approximate critical nuclearities (N_c(A-B) = the nuclearity at which structure A and structure B have the same energy) calculated using the fitted coefficients.[45] These values are generally very high, when compared to other potentials,[24] though the nuclearity at which bcc becomes favoured over icosahedral (at around 2000 atoms) is relatively low. In fact bcc is preferred over fcc and dec even at very low cluster sizes. Although the plots of E_b against $N^{-1/3}$ (Figure 6) look approximately linear, if we fit them using straight lines (E_b = **a** + **b**$N^{-1/3}$) then: the bulk limit cohesive energies (**a**) are overestimated by up to 1%; the extrapolated fcc line never crosses the ico line; and the N_c value for the ico-bcc crossover is much higher (> 4000). This emphasises the importance of using the theoretically justified cubic (in $N^{-1/3}$) equation 14 to fit the calculated E_b values.

We have also fitted the binding energies reported by U&W for ico, dec and fcc model transition metal clusters (of metals crystallising with the fcc structure) using pairwise LJ, 2+3-body LJ+AT, and the many-body SC potentials.[24] We found that, as long as the 3-body (AT) contribution is not large, the explicit 2+3-body LJ+AT potentials gave qualitatively very similar results to the 2+3-body GJM potential (with the same signs and approximate magnitudes for **a**-**d**). The SC potentials give the same signs of the coefficients as the GJM potential, but with **b/a**<1, which is consistent with the known underestimation of surface energies by SC many-body potentials.[46] The LJ pair potentials, on the other hand give much higher **b/a** ratios (corresponding to higher surface energies) and positive **c** values.

Comparing our critical (cross-over) nuclearities, N_c for ico-dec, ico-fcc and dec-fcc, with those obtained by U&W, we find that ours are nearly an order of magnitude higher than for the LJ pair potential and higher still when compared with the LJ+AT potentials, since the addition of the 3-body AT term has been shown to lead to a dramatic reduction in N_c. The SC potentials tend to give even lower (probably too low) cross-over nuclearities, due to the many-body contributions which are implicitly included in this potential *via* the term in the square root of the atomic density.[47] Similar results were obtained by Marville and Andreoni using a Finnis-Sinclair potential[30] (of which the Sutton-Chen potential is a particular variant)[36] for the bcc metals Ta, Mo and W.[29] They predicted bcc clusters to be more stable than fcc or ico for N>100 and fcc to be more stable than ico for: N>4000 (Ta); N=923 (Mo); and N=147 (W).[29] The high values that we obtain for the N_c values between the 12-coordinate structures, reflects the long range nature of our potential, since U&W have shown that longer range potentials have higher cross-over nuclearities.[24] It should be noted that the cross-over to bcc being the most stable structure is predicted to occur at quite low nuclearity (N_c(ico-bcc) ~ 2000) which is comparable with the N_c values for the ico-fcc crossover using LJ+AT potentials. This reflects the fact that the GJM potential was optimised by fitting the lattice dynamical properties of bulk iron,[19] which is most stable, at low temperatures, in the bcc form. Experimental evidence for structural phase transitions as a function of size for clusters is rather ambiguous, but electron diffraction studies on argon clusters have led Farges *et al.* to postulate a transition from icosahedral to fcc (cuboctahedral) geometries at around 750 atoms.[48]

(c) Geometric fcc-like shell clusters with non-spherical topologies

Since the cuboctahedral fcc clusters we have considered so far expose both {111} and {100}-type faces and since it is the relatively high number of atoms in the non-close-packed {100} faces which destabilise the clusters, we have also looked at modified fcc ("mod") clusters formed by increasing the size of the more stable {111} faces at the expense of the less stable {100} faces. In effect this involves a surface reconstruction of the cluster (though the magic numbers are now different to those for cuboctahedral clusters). An example of a series of four mod clusters is shown in Figure 7. These clusters are less spherical than their cuboctahedral counterparts and (with the exception of octahedral Fe_{19}) have truncated-octahedral geometries. The cluster binding energies of the mod clusters are listed in Table 7 and plotted against N in Figure 8, from which it can be seen that growing the {111} faces at the expense of the {100} faces leads to increased cluster stability relative to the cuboctahedral (fcc) clusters (in this size regime the mod clusters are comparabe in stability to the bcc structures). This cannot, however be carried on indefinitely for two reasons:

(i) as the modified fcc clusters are less spherical than the cuboctahedral ones, the percentage of surface atoms is actually higher.

(ii) fcc-type clusters with only {111} faces are octahedra. Although octahedral shell clusters only have 8 faces, they also have apical atoms with coordination numbers of only 4.

Thus it can be seen that at high nuclearities the difference between the modified fcc and cuboctahedral fcc curves is smaller than at low nuclearities. Indeed, fitting the polynomial of Equation 14 to this plot gives the following coefficients (in eV): **a** = 4.249; **b** = -4.394; **c** = -1.517; **d** = 1.823. The fit is exact as 4 coefficients are being fitted to only 4 pieces of data. Comparing these values with those obtained by fitting the cuboctahedral cluster (fcc) binding energies (Table 6) reveals that the bulk limit (**a**) is actually smaller for the modified fcc clusters, though as expected the magnitudes of the (negative) surface and edge corrections (**b** and **c** respectively) are also smaller.

(d) Normal Mode Analysis for Geometric Shell Clusters

Analysis of the normal mode vibrational frequencies of the pseudo-spherical shell clusters reveals that the ico clusters have all real frequencies at all nuclearities, indicating that they are (at least) local minima on the PE surface. The bcc clusters are all metastable (with respect to the ico clusters) in that they are again minima but lie at higher energies, with the exception of bcc-Fe_{15} which has a single imaginary frequency, thereby making it a true transition state on the PE surface. The fcc clusters are all true transition states, with the magnitude of the single imaginary frequency decreasing with increasing nuclearity. U&W have previously studied the nature of the rearrangement mechanism for inter-converting ico shell clusters via fcc (cuboctahedral) transition states.[22] The fact that the imaginary frequancy becomes smaller as N increases mirrors the decrease in energy difference between ico and fcc clusters, since this frequency should become real at high nuclearities, where the fcc clusters become stable relative to ico geometries. The dec clusters also have one or more imaginary frequencies at all nuclearities, indicating that they are transition states (or higher order saddle points) on the PE surface. These findings are in general agreement with those of U&W using LJ and SC potentials and for some of the LJ+AT potentials, with the main difference being that they predict the fcc and dec clusters to become metastable at much lower nuclearities.[24] This is consistent with the much smaller stability cross-over points calculated using these alternative potentials, as mentioned above.

As U&W have demonstrated, capping the faces of transition state structures or growing more stable surfaces at the expense of less stable ones can lead to metastable structures with all real vibrational frequencies.[22] Our calculations on the non-spherical mod clusters are consistent with their findings, as we predict all of these structures to be metastable.

5. Discussion: Comparison with Experimental Data and Electronic Structure Calculations

The results of our PEF calculations on small iron clusters can be tested against the limited amount of experimental data[4-8] and more abundant results from *ab initio* calculations which are available for these species.[10-13] Thus, for Fe_3 we obtain an equilateral triangle (**3**) as the most stable structure, in agreement with Mössbauer experiments,[6] and the results of *ab initio* calculations.[11] Our tetrahedral geometry for Fe_4 (**4**) and trigonal bipyramidal structure for Fe_5 (**5**) are also in agreement with the *ab initio* calculations of a number of groups.[11-13]

For small clusters (2-20 atoms), the GJM potential favours polytetrahedral structures, with this growth mode eventually leading to clusters with local icosahedral structure. There have been a number of experimental studies of the stability and reactivity of small iron clusters ($N<20$) which have enabled cluster geometries to be inferred. Armentrout and co-workers have investigated the collision-induced dissociation of iron cluster cations and, with the aid of known cluster IPs have calculated the dissociation energies (by single atom evaporation) of neutral Fe_N clusters.[8] In the region N=2-19, they found local maxima in dissociation energy for N = 6, 7, 13, 15 and 19 and minima at N = 8, 14 and 18. The 7, 13, 19 sequence would be consistent with our icosahedral growth pattern, but they have suggested that the stability of N = 6, 15 and 19 can be explained using a model wherein they are all based on a six atom octahedral core (our predicted geometry for N=6) with N=15 being a fragment of the bcc structure and N=19 a fragment of fcc. On the basis of reactivity studies of gas phase iron clusters with small molecules (*e.g.* H_2, H_2O, NH_3), Riley and co-workers have also suggested that Fe_{15} has the bcc structure and Fe_{19} the fcc geometry.[7]

Christensen and Cohen, employing an Effective Medium Theory+Tight Binding model,[13a] for clusters up to Fe_{18}, have predicted the following high-symmetry ground state structures: Fe_{10} = bicapped square antiprism (D_{4d}); Fe_{12} = icosahedron (I_h); Fe_{15} = centred bicapped hexagonal antiprism (D_{6d}), with low-symmetry structures for Fe_{11}, Fe_{13} and Fe_{14}. These results are at variance with our calculations, for which the most stable geometries in this size regime are predicted to be based on the Fe_{13} centred icosahedron (**13**) either by removing outer atoms or by adding capping atoms.

We found previously that, for small clusters (Fe_2-Fe_7) the GJM potential leads to a consistent underestimation of the cluster binding energies and vibrational frequencies and an overestimation of the equilibrium bond lengths, compared with calculated and experimental values.[19] This is because small Fe clusters possess a considerable amount of multiple bond character and our potential is optimised to the solid, where the average bond order is much smaller. The discrepancies between our predicted most stable geometries and experimental results and/or electronic structure calculations for clusters with 10-20 atoms may also be attributed to the neglect, in the GJM potential, of any explicit electronic information. Such differences are expected to becomes less significant for larger clusters where the average environment (at least the coordination number if not the exact geometry) becomes closer to that of the bulk, for which the potential was parameterised.

For large geometric shell clusters, the GJM potential favours icosahedral and decahedral structures slightly over bcc and somewhat more over fcc structures. The closeness of the icosahedral and bcc cluster binding energies (in particular) indicate that in the size regime $10<N<1000$ we would expect to find a number of cluster isomers very closely spaced in energy and this is borne out by the results of experiments on gas phase iron clusters.

Experimental evidence for magic number clusters of iron is sparse. In contrast to cobalt and nickel, where the intensities of peaks in the mass spectra of gas phase clusters correspond to species with icosahedral shell structure, Pellarin *et al.* have shown that iron clusters in the range N = 50-800 exhibit no clear cut behaviour.[6d] Thus for $50 \leq N \leq 200$ the results, while being similar to those for Co and Ni and supporting icosahedral structures, were found to depend on source conditions. They also suggested the possibility of competion between icosahedral geometric shell structures and *jellium* electronic-shell structures (implying liquid-like iron clusters) in this size range. For larger clusters the mass spectra are highly structured, but peak intensities are again strongly dependent on source conditions, indicating competion between structural isomers.[6d] The occurence of numerous isomers with comparable energies has also been suggested by Riley and co-workers (on the basis of reactivity studies on iron clusters $2<N<165$),[7] Yang and Knickelbein (near-threshold ionization cross section studies)[6c] and Armentrout and co-workers (collision-induced cluster dissociation).[8]

The small differences in relative energies which we have calculated for the (geometric shell) large iron clusters is in broad agreement with these experimental findings. However the experimental evidence presently available does not allow a more conclusive statement to be made as to whether our predictions are correct. The study here reported has involved the calculation of static properties at 0 Kelvin, ignoring temperature effects and cluster dynamics. Uppenbrink and Wales, using a SC potential for Au_{55}, have found that there are a number of low symmetry glass-like or amorphous structures which (for this potential) have lower energies than the high symmetry (metastable) MNCs.[49] In order to establish whether such behaviour is predicted for iron clusters, using the GJM potential, we are currently investigating the dynamics of GJM-shell clusters.

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Figure Legends

Figure 1. Polyhedra defining the ico, dec, fcc and bcc classes of shell clusters.

Figure 2. The outer shells of 5-shell ico, dec, fcc and bcc clusters. Geometries are idealised (*i.e.* before radial cluster relaxation) and the fcc and bcc clusters have all nearest neighbour bond lengths equal. All clusters in this paper have been drawn using XMOL (Research Equipment Inc., Minnesota Supercomputer Center, USA, 1993).

Figure 3. Optimised geometries for Fe_2-Fe_{20} (using the GJM potential). Descriptions and binding energies are given in Table 2. Bonds to encapsulated atoms have been omitted for clarity.

Figure 4. Plot of binding energy (E_b) against number of atoms (N), for the most stable cluster geometries for Fe_2-Fe_{20}.

Figure 5. Plot of binding energy (E_b) against number of atoms (N), for radially optimised shell clusters Fe_N.

Figure 6. Plot of binding energy (E_b) against $N^{-1/3}$ for radially optimised shell clusters Fe_N.

Figure 7. Modified fcc shell clusters with larger {111} and smaller {100} faces than the cuboctahedral clusters.

Figure 8. Plot of binding energy (E_b) against number of atoms (N), for radially optimised modified fcc ("mod") shell clusters Fe_N and comparison with ico and fcc clusters.