

## Structures of large Morse clusters

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The binding energy of atoms interacting via pairwise Morse potentials is calculated by several methods for large clusters of face-centered cubic (fcc) and icosahedral structures: by numerical calculations for bulk particles, by direct numerical calculations for numbers of atoms  $n = 561-923$ , and by analytical methods using perturbation theory. A phase diagram is constructed for a wide range of cluster sizes, which links the adjustable range parameter of the Morse potential to the cluster energy along the curve corresponding to the set of conditions for which the energies of the fcc and icosahedral structures are equal. © 1999 American Institute of Physics.

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### I. INTRODUCTION

The optimal cluster structure depends not only on the character of interaction of its atoms, but also on cluster size. The variation of cluster size can lead to changes of the most stable cluster structure. We consider this problem in the case of a pair interaction between atoms for which the optimal cluster structure is icosahedral for small cluster sizes and the face-centered cubic (fcc) structure for large sizes. It is convenient to analyze the transition between these structures using the Morse interaction potential for pairwise interactions between atoms. We take it in the form

$$U(R) = D(e^{-2\alpha(R-R_e)} - 2e^{-\alpha(R-R_e)}), \quad (1)$$

where  $R$  is the distance between atoms,  $R_e$  is the equilibrium distance between atoms in the diatomic molecule,  $D$  is the dissociation energy of the classical diatomic molecule, which we later set equal to 1, and  $\alpha$  (or  $\alpha R_e$ ) is the adjustable range parameter. Depending on the value of this parameter, one can change the relation between short-range and long-range parts of the interaction potential. Hence, it is convenient to use this interaction potential for the analysis of the competition of structures.<sup>1</sup> Indeed, for a wide range of cluster sizes one can find a value of the parameter  $\alpha$  for which cluster energies coincide for the icosahedral and most stable fcc structures. The determination of the phase diagram<sup>1</sup>—the dependence  $\alpha(n)$ , where  $n$  is a number of cluster atoms is the goal of this paper.

Note that competition of the icosahedral and fcc structures is sensitive to aspects of the form of the pair interaction potential between atoms, particularly to its range. Real clusters of inert gases exhibit the transition from the icosahedral to the fcc structure in the size range of 1000–3000 cluster atoms.<sup>2-4</sup> In the case of Lennard-Jones interactions between atoms, the cuboctahedral structure, one of the fcc cluster structures, becomes more stable energetically than the icosahedral structure at a number of cluster atoms  $n \sim 10^4$ .<sup>5,6</sup> The

transition between icosahedral and fcc structures in the case of a short-range interaction between atoms takes place at  $n = 200-500$ .<sup>7,8</sup> Such sensitivity of the competition among structures to form the interaction potential requires a more careful analysis of this problem, which is our aim in this paper.

We exclude from consideration any hexagonal structures of clusters. This structure competes with the fcc structure at small cluster sizes,<sup>9,10</sup> where the icosahedral structure is the most stable, but in the region of competition where the fcc and icosahedral structures have comparable energies, the fcc structure has a higher average binding energy per atom than the hexagonal. Next, we examine clusters with icosahedral cores. Such clusters may have a surface layer that fills with either an icosahedral or a fcc structure,<sup>2,3,11</sup> depending on the degree of filling of the outer layer. We choose the structure of that layer with the higher total binding energy.

The growth of fcc clusters proceeds by filling its plane facets.<sup>9,12</sup> The core of a fcc cluster may or may not have a central atom. From these, we choose the fcc structure with the higher total binding energy. Thus, comparing the fcc and icosahedral structures, we take the optimal configuration of atoms with the maximum cluster binding energy, given the number of atoms for each structure.

We shall also consider large systems of atoms interacting through pairwise Morse potentials at zero temperature. These are designated as “bulk” because they are large enough that the binding energy per added particle in the interior is constant. In the present treatment, we neglect the entropic contributions that certainly play an important role in determining the relative stability of different structures at moderate temperatures. However, we suppose that in many cases, the low-temperature, energy-determined limit will be reflected in the behavior of clusters under attainable conditions. Moreover, the role of energy is, in any case, a necessary if not sufficient step in solving the full problem of stability. We take optimal structures of such systems and calculate their specific spatial and surface energy. (We must

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work with clusters large enough that these quantities are unambiguous.) The “magic number” icosahedral structures consist of bound atoms that form filled icosahedra,<sup>13</sup> while for the fcc structure the particles form truncated octahedra. We use the method<sup>14</sup> for constructing structures such as truncated octahedra and calculate their spatial and surface energies. The relations among lengths of edges of this figure depend on the form of the interaction potential.<sup>14</sup> As a result, we find the total binding energy of atoms  $E$  for each structure, which has the following asymptotic expansion at large numbers of atoms  $n$ :<sup>15</sup>

$$E = \epsilon_{\text{sub}}n - An^{2/3}. \quad (2)$$

Here  $\epsilon_{\text{sub}}$  is the bulk binding energy per atom, and  $A$  is the specific surface energy. It is clear that the optimal configuration of atoms of a large icosahedral cluster approaches that of the completed icosahedron.

## II. SPECIFIC ENERGY OF BULK MORSE CRYSTALLITES

First, we calculate the specific spatial energy of a face-centered cubic (fcc) bulk system. The total binding energy of atoms in a system of many bound atoms with a pair interaction of atoms is

$$E = \frac{1}{2} \sum_k n_k U(ka), \quad (3)$$

where  $a$  is the distance between nearest neighbors, and  $n_k$  is the number of bonds of a length  $ka$ . The factor  $\frac{1}{2}$  takes into account that each bond involves two atoms.

We introduce the sublimation energy  $\epsilon_{\text{sub}}$ , which is the mean binding energy, per atom, of the crystalline cluster:

$$\epsilon_{\text{sub}} = E/n = \frac{1}{2} \sum_k n_k U(r_k), \quad (4)$$

where  $r_k = ka$  is the distance from a reference atom to the  $k$ th atom, and  $n_k$  is the number of atoms at this distance from the reference atom. Using the Morse interaction potential (1), we represent the sublimation energy of the composite particle in the form

$$\epsilon_{\text{sub}} = \exp(\alpha R_e) f(\alpha a) - \frac{1}{2} \exp(2\alpha R_e) f(2\alpha a), \quad (5)$$

where  $\epsilon_{\text{sub}}$  is expressed in the binding energy  $D$  per bond, and

$$f(\alpha a) = \sum_k n_k \exp(-\alpha r_k). \quad (6)$$

Let us introduce the derivative of this function,

$$f'(\alpha a) = \frac{df(\alpha a)}{d(\alpha a)} = - \sum_k (n_k r_k / a) \exp(-\alpha r_k).$$

Optimizing the sublimation energy with respect to  $a$ , the distance between nearest neighbors, we find that

$$\exp(\alpha R_e) = f'(\alpha a) / f'(2\alpha a). \quad (7)$$

Correspondingly, the sublimation energy of the bulk is

TABLE I. Parameters of shells of the fcc structure;  $r^2 = k^2 a^2$  is the square of the distance from the center where  $a$  is the distance between nearest neighbors, and  $n_k$  is the number of shell atoms.

Shell	$r^2/a^2$	$n_k$	Shell	$r^2/a^2$	$n_k$
011	1	12	044	16	12
002	2	6	334	17	24
112	3	24	035	17	24
022	4	12	006	18	6
013	5	24	244	18	24
222	6	8	116	19	24
123	7	48	235	19	48
004	8	6	026	20	24
114	9	24	145	21	48
033	9	12	226	22	24
024	10	24	136	23	48
233	11	24	444	24	8
224	12	24	055	25	12
015	13	24	017	25	24
134	13	48	345	25	48
125	15	48	046	26	24

$$\epsilon_{\text{sub}} = \frac{f'(\alpha a)}{f'(2\alpha a)} f(\alpha a) - \frac{1}{2} \left( \frac{f'(\alpha a)}{f'(2\alpha a)} \right)^2 f(2\alpha a). \quad (8)$$

It is convenient to divide the function  $f(\alpha a)$  in parts:<sup>1</sup>

$$f(\alpha a) = f_{\text{nn}}(\alpha a) + f_{\text{nnn}}(\alpha a), \quad (9)$$

where  $f_{\text{nn}}$  and  $f_{\text{nnn}}$  account for the interaction of nearest neighbors and nonnearest neighbors, respectively, in formula (6), so that for a bulk system with a fcc structure, we have

$$f_{\text{nn}}(\alpha a) = 12 \exp(-\alpha a).$$

Then the specific binding energy of a bulk system, i.e., mean energy per atom, takes the form<sup>1</sup>

$$\epsilon_{\text{sub}} = \epsilon_{\text{nn}}(R_e) + \epsilon_{\text{nnn}}(R_e) + \epsilon_{\text{str}}, \quad (10)$$

where  $\epsilon_{\text{nn}}(R_e)$  and  $\epsilon_{\text{nnn}}(R_e)$  are the interaction energies between nearest and non-nearest neighbors, correspondingly, and the strain energy is equal to

$$\epsilon_{\text{str}} = \epsilon_{\text{sub}}(a) - \epsilon_{\text{sub}}(R_e), \quad (11)$$

where  $a$  is the optimal distance between nearest neighbors, determined by formula (7), and corresponds to the maximum binding energy of the crystalline cluster.

In order to determine the functions  $f_{\text{nn}}(\alpha a)$  and  $f_{\text{nnn}}(\alpha a)$ , it is necessary to choose a distribution of atoms in shells around a reference atom for the corresponding bulk structure. Table I contains these data and indicates the shells with a notation for the fcc crystal structure taken from Ref. 16, so that the numbers  $klm$  of a shell denote coordinates  $xyz$  of one atom of this shell in units  $a/\sqrt{2}$ , where  $a$  is the distance between nearest neighbors. Dividing atoms in shells, we take into account the symmetry of the fcc structure with respect to transformations:

$$x \leftrightarrow y \leftrightarrow z: \quad x \leftrightarrow -x; \quad y \leftrightarrow -y; \quad z \leftrightarrow -z. \quad (12)$$

Table II contains values of the sublimation energies for the Morse crystal of the fcc structure that are obtained by the above procedure.

TABLE II. Parameters of the fcc cluster with Morse interactions between atoms.

$\alpha a$	$\alpha R_e$	$f(\alpha a)$	$-df(\alpha a)/d(\alpha a)$	$f(\alpha a) \times \exp(\alpha a)$	$\epsilon_{\text{sub}}/D$
2	3.03	3.87	6.47	28.6	21.3
3	3.57	0.910	1.17	18.3	12.2
4	4.31	0.274	0.311	14.9	8.94
5	5.17	0.0911	0.0975	13.5	7.52
6	6.10	0.0318	0.0330	12.8	6.84
7	7.06	0.0114	0.0116	12.5	6.47
8	8.03	0.004 12	0.004 17	12.3	6.29
9	9.02	0.001 503	0.001 514	12.2	6.18
10	10.01	$5.499 \times 10^{-4}$	$5.523 \times 10^{-4}$	12.1	6.11

The symmetry of the cluster's hexagonal structure corresponds to reflection of the system with respect to the initial plane  $xy$  and a turn about the axis  $z$  by angle  $\pi/3$ . Take an atom as the origin and construct atomic shells around it so that atoms of one shell can exchange their positions as a result of the above transformation. Numbering layers of this structure, we obtain positions of atoms of the hexagonal structure that are represented in Table III.<sup>16</sup> Note that the hexagonal structure has a lower symmetry than the fcc, so that the average number of atoms of one shell of the hexagonal structure is smaller than that of the fcc structure.

Now let us consider a large icosahedral cluster with filled shells and Morse interactions between atoms. The icosahedral surface is like the hexagonal when positions of atoms with respect to a test atom are those given in Table III. Let us take into account that the distance between neighboring icosahedral layers is  $\sqrt{R^2 - R_0^2}/3$  and the surface area per atom is equal to  $R_0^2\sqrt{3}/2$  where  $R_0 = 1.051R$  is the distance between nearest neighbors of the same layer, and  $R$  is the distance between nearest neighbors of neighboring layers. Then we take the distance between atoms of an icosahedral structure in the same way we carried out the evaluation for the hexagonal structure, and change the distance (squared) between two atoms  $ma^2$  by the value  $R^2 + (m-1)R_0^2$  for atoms of the first layer, by the value  $4R^2 + (m-4)R_0^2$  for atoms of the second layer, by the value  $9R^2 + (m-9)R_0^2$  for atoms of the third layer, by  $16R^2 + (m-16)R_0^2$  for atoms of the fourth layer, etc. Table IV lists values of the sublimation energies for icosahedral bulk systems with Morse potentials.

### III. SURFACE ENERGY OF BULK MORSE SYSTEMS OF ATOMS

In order to find the optimal form of a bulk crystal of a given structure, it is necessary to find its surface energy. First we find the optimal bulk structure of the fcc crystal as a function of the parameter  $\alpha$  of the Morse potential. To do this, we use the method<sup>14</sup> of constructing a truncated octahedron. Then we take a cube of the length  $2L$  and the frame of axes where the direction of its planes is  $\{100\}$  (according to usual notation<sup>17</sup> for crystal planes). Let us cut off regular triangle pyramids near each cube vertex by cutting planes in the direction  $\{111\}$  and its equivalents. Let us introduce a parameter  $\beta$  such that  $\beta L$  is the length of the base edges of the pyramids. In our case, this parameter ranges from 1 to 2.

As a result of transformations, we obtain families of various polyhedra. A figure so formed has 14 facets, of which 6 have the direction  $\{100\}$  or equivalent, and 8 have the direction of the cutting plane  $\{111\}$  or its equivalent. The case  $\beta = 1.5$  corresponds to formation of the regular truncated octahedron whose surface consists of eight regular hexagons and six squares.

The surface energy of the truncated octahedron has the form

$$E_{\text{sur}} = n_{100}\epsilon_{\text{sur}}^{100}S_{100} + n_{111}\epsilon_{\text{sur}}^{111}S_{111}, \quad (13)$$

where  $S_{100} = 6s_{100} = 12(2 - \beta^2)L^2$  is the total area of the surface squares, and  $S_{111} = 8s_{111} = 4\sqrt{3}(6\beta - 2\beta^2 - 3)L^2$  is the total area of the hexagons. These expressions are valid for  $1 < \beta < 2$ ;  $n_{100}$  and  $n_{111}$  are the numbers of the surface atoms on squares and hexagons of the surface, and  $\epsilon_{\text{sur}}^{100}$ ,  $\epsilon_{\text{sur}}^{111}$  are the specific surface energies of the system. Because the number density of atoms for a close-packed structure is  $\sqrt{2}/a^3$ , the total number of atoms  $n$  in our cluster crystallite is  $V\sqrt{2}/a^3$ , where  $V = (8\beta^3/3 - 12\beta^2 + 12\beta + 4)L^3$  is the volume of the figure. Thus, we obtain the asymptotic expression for the surface energy of our system:

$$E_{\text{sur}} = An^{2/3},$$

where

$$A = [3(2 - \beta)^2\epsilon_{\text{sur}}^{100} + \sqrt{3}(6\beta - 2\beta^2 - 3)\epsilon_{\text{sur}}^{111}] \times (\beta^3/3 - 3\beta^2/2 + 3\beta/2 + 1/2)^{-2/3}. \quad (14)$$

To determine the specific surface energies of the crystallite  $\epsilon_{\text{sur}}^{100}$  and  $\epsilon_{\text{sur}}^{111}$ , let us divide the infinite fcc crystal in two parts by a plane: either  $\{100\}$  or  $\{111\}$ . The specific surface energy corresponds to the interaction potential of these parts per unit area. Let us denote by  $U_k$  the interaction energy of a test atom with all the atoms of the  $k$ th shell around the test atom, which defines the zeroth shell or origin. Then the specific surface energy, is

$$\epsilon_{\text{sur}} = \frac{1}{2} \sum_{k=1}^{\infty} kU_k/s, \quad (15)$$

where  $s$  is the area per atom; again, the factor of  $1/2$  appears because each bond involves two atoms.

Its form may not make this obvious, but Eq. (15) accounts for all the interaction energy for a plane bulk surface. To determine the surface energy of a macroscopic surface, we divide an infinite crystal in two parts by a plane and calculate the interaction potential between layers parallel to this plane. Then we take a test atom on the surface of one part and, moving it deep in this part, calculate the interaction potential of this atom with all the layers of the other part of the crystal. One can see that we obtain the same interaction potential, for example, when a test atom is located on one surface and interacts with the penultimate layer below the other surface when it is located in the second layer of one crystal piece and interacts with the surface layer of the other. Denoting the interaction potential of a test atom with the penultimate layer by  $U_2$ , we account for this fact, repeating the potential  $U_2$  twice in the formula for the total interaction potential. In the same way, we account for the interaction

TABLE III. Parameters of shells of the hexagonal structure;  $r^2=k^2a^2$  is the square of the distance from the center, where  $a$  is the distance between nearest neighbors and  $n_k$  is a number of shell atoms. The position of one layer for a typical shell is shown.

Layer	$r^2/a^2$	$n_k$	Layer	$r^2/a^2$	$n_k$
0	1	6	1	9	6
1	1	6	2	29/3	24
1	2	6	1	10	12
2	8/3	2	3	31/3	12
0	3	6	4	32/3	2
1	3	12	1	11	12
2	11/3	12	3	34/3	6
0	4	6	2	35/3	12
1	5	12	4	35/3	12
2	17/3	12	0	12	6
1	6	6	3	37/3	12
3	19/3	6	0	13	12
2	20/3	12	1	13	12
0	7	12	4	41/3	12
1	7	12	3	43/3	6
3	22/3	6	2	44/3	12
3	25/3	12	4	44/3	12
0	9	6	1	15	12

potential of a test atom located on the surface with the  $k$ th layer,  $U_k$ ,  $k$  times as we move a test atom deep inside the first crystal part. As a result, we obtain formula (15).

In the case of the Morse interaction potential (1), this formula gives the specific surface energy:

$$\epsilon_{\text{sur}} = [G(\alpha a)\exp(\alpha R_e) - \frac{1}{2}G(2\alpha a)\exp(2\alpha R_e)]/s. \quad (16)$$

Here  $a$  is the distance between nearest neighbors,  $R_e$  is the equilibrium distance for the diatomic, and  $s$  is the surface area per atom; we set  $D=1$  in formula (1) and

$$G(\alpha a) = \sum_{i,j} kn_{ik} \exp(-\alpha r_{ik}), \quad (17)$$

where  $r_{ik}$  is a distance from a test atom to the  $i$ th atom of the  $k$ th layer and  $n_{ik}$  is a number of such atoms.

Tables V and VI contain the numbers of atoms in {100} and {111} surfaces whose distance from a test atom satisfies  $r_{ik}^2 \leq 12$ . For the {100} surface, the distance between neighboring layers is  $a/\sqrt{2}$ , and the area per surface atom is  $s = a^2$ . For the {111} surface, these parameters are  $a\sqrt{2/3}$  and  $a^2\sqrt{3}/2$ , respectively. We are restricted in the sum (17) by  $r_{ik}^2 \leq 12$ , valid for  $\alpha$  not too small. Let us estimate the accu-

TABLE IV. Parameters of an icosahedral bulk system of atoms with Morse interactions between atoms.

$\alpha R$	$\epsilon_{\text{sub}}$	$G(\alpha R)$	$A$	$n_*$
2	12.16	1.176	28.1	2680
3	9.60	0.303	18.3	1260
4	8.07	0.0889	13.0	1260
5	7.16	0.0288	10.2	1700
6	6.62	$9.93 \cdot 10^{-3}$	8.56	1930
7	6.27	$3.56 \cdot 10^{-3}$	7.64	1080
8	6.03	$1.31 \cdot 10^{-3}$	7.05	260(116)
10	5.70	$1.82 \cdot 10^{-4}$	6.34	62(41)
12	5.13	$2.57 \cdot 10^{-5}$	5.82	26(23)

TABLE V. Distances of nearest-neighbor atoms around a test atom of a {100}-surface of the fcc structure. The area per single surface atom is  $s = a^2$ .

$r_{ik}^2/a^2$	One-layer	Two-layer	Three-layer	Four-layer
1	1	...	...	...
2	...	1	...	...
3	8	4	...	...
4	...	4	...	...
5	1	...	4	...
6	...	4	...	...
7	8	8	8	...
8	...	...	...	1
9	8	...	4	4
10	...	4	...	4
11	...	...	8	...
12	...	8	...	4

racy of this approximation for the {100} surface. The contribution in the sum (17) owing to the interaction of nearest neighbors is  $G_{\text{nn}}(\alpha a) = 4 \exp(-\alpha a)$ . We estimate the contribution  $\Delta G$  due to the interaction with further atoms  $r_{ik}^2 \geq 13$  by replacing the sum (17) by an integral. Then we obtain

$$\Delta G/G_{\text{nn}} = 58 \exp(-2.6\alpha a)/(a\alpha).$$

In particular, for  $\alpha a = 3$  this formula gives  $\Delta G/G_{\text{nn}} = 0.008$ , and since we are guided by higher values of this parameter, one can neglect the contribution of  $\Delta G$  in the sum (17).

From this, one can find the specific energy, the energy per surface atom,

$$g(\alpha a) = \exp(\alpha R_e)G(\alpha a) - \frac{1}{2} \exp(2\alpha R_e)G(2\alpha a). \quad (18)$$

In particular, in the case of a short-range interaction between atoms, the value  $g$  is one-half the energy of bonds between nearest neighbors outside the surface i.e., it is  $g_{100} = 2$  for a {100} surface and  $g_{111} = \frac{3}{2}$  for a {111} surface. These values correspond to asymptotic values of  $g$  in the limit of large  $\alpha a$ . Values of the functions  $G(\alpha a)$ , and  $g(\alpha a)$  for the fcc surfaces considered here are given in Table VII. Note that the connection between the nearest-neighbor distance  $a$  and the equilibrium distance of diatomic  $R_e$  is taken from Table II.

TABLE VI. Distances of nearest atoms to a test atom of a {111} surface of the fcc structure. The area per surface atom is  $s = a^2\sqrt{3}/2$ .

$r_{ik}^2/a^2$	One-layer	Two-layer	Three-layer	Four-layer
1	3	...	...	...
2	3	...	...	...
3	6	3	...	...
4	...	3	...	...
5	6	6	...	...
6	3	...	1	...
7	6	6	6	...
8	...	3	...	...
9	3	6	6	...
10	6	...	...	...
11	6	3	6	3
12	...	3	6	3

TABLE VII. Parameters of a bulk crystal with a fcc structure, with Morse interactions between atoms.

$\alpha a$	$\alpha R_e$	$G_{100}$	$G_{111}$	$g_{100}$	$g_{111}$	$A$	$\beta_{opt}$
2	3.03	2.00	1.70	37.6	32.1	155	1.30
3	3.57	0.387	0.321	11.3	9.52	46.4	1.33
4	4.31	0.103	0.0832	5.53	4.57	22.4	1.35
5	5.17	0.0322	0.0255	3.64	2.94	14.5	1.39
6	6.10	0.0109	0.008 50	2.85	2.28	11.3	1.41
7	7.06	0.003 84	0.002 96	2.48	1.95	9.69	1.43
8	8.03	0.001 38	0.001 06	2.25	1.74	8.71	1.45
10	10.01	0.000 184	0.000 139	2.08	1.59	7.96	1.48
12	12.00	0.000 024 7	0.000 018 6	2.02	1.52	7.66	1.49

We now show that the optimal configuration of the fcc crystal for a short-range atom–atom interaction potential is one in which the crystalline surface contains eight regular hexagons and six squares. Other types of atom–atom interactions lead to different configurations that minimize the surface energy for a given number of atoms. Below we determine the optimal crystalline configuration as a function of the Morse parameter  $\alpha$  on the basis of the condition that the specific surface energy (14) of the crystalline is a minimum. It has the form

$$A = \frac{2[3(2-\beta)g_{100} + 6(6\beta - 2\beta^2 - 3)g_{111}]}{(4\beta^3/3 - 6\beta^2 + 6\beta + 2)^{2/3}}, \quad (19)$$

where  $g_{100}$  and  $g_{111}$  are the specific surface energies per surface atom (18) for the corresponding plane of facets. In the case of a short-range interaction between atoms that allows us to include only interactions between nearest neighbors, those parameters are  $g_{100} = 2$  and  $g_{111} = \frac{3}{2}$ , and the specific surface energy has a minimum at  $\beta = \frac{3}{2}$ , where its value is  $A = 2^{1/3} \cdot 6$ . This occurs for large values of  $\alpha$ , the Morse parameter.

At any value of the parameter  $\alpha$ , the optimal value  $\beta$  differs from  $\frac{3}{2}$ . Below we assume this value  $\beta_{opt}$  to be close to  $\frac{3}{2}$ , so that one can expand the expression for  $A$  in powers of a small parameter  $\beta - \frac{3}{2}$ . Then the specific surface energy takes the form

$$A = 2^{1/3} \cdot 6 \cdot [g + \Delta g/2 + g(\beta - 3/2)^2/4 + 1.5\Delta g(\beta - \frac{3}{2})], \quad (20)$$

where  $g = g_{100}/4 + g_{111}/3$  and  $\Delta g = g_{111}/3 - g_{100}/4$ .

From this formula it follows that the optimal value of  $\beta$  and the minimum value of the specific surface energy satisfy

$$\beta_{opt} - \frac{3}{2} = -3\Delta g/g, \quad (21)$$

$$A = 6 \cdot 2^{1/3} \cdot [g + \Delta g/2 - 9\Delta g^2/(4g)].$$

Using values of  $g_{100}$  and  $g_{111}$  of Table VII, we find the values of this formula given in Table VII. Note that  $\beta_{opt} < 1.5$ , i.e., the optimal crystalline figure, differs from a regular truncated octahedron such that edges connecting squares with hexagons are longer than edges joining two hexagons.

All the facets of an icosahedral crystal are equivalent, so that parameters of the icosahedral surface are expressed through one value  $g(\alpha R)$ , where  $R$  is the distance between nearest neighbors in neighboring layers. Considering the icosahedral surface as a distorted hexagonal face, we calcu-

late the specific surface energies given in Table IV. The connection between specific surface energies has this form for an icosahedral cluster:

$$A = \frac{n_{sur}}{n^{2/3}} [G(\alpha R)e^{\alpha R} - \frac{1}{2}G(2\alpha R)e^{2\alpha R}] = 90^{1/3}g(\alpha R), \quad (22)$$

where  $n_{sur}$  is the total number of surface atoms and  $n$  is the total number of atoms in the cluster.

In the case of an atom–atom interaction whose range is short enough to allow us to consider only interactions between nearest neighbors, we have

$$g = \frac{3}{2}[1 - \alpha^2(R_e - R)^2], \quad \alpha R \gg 1, \quad \alpha(R_e - R) \ll 1. \quad (23)$$

Using  $R = 0.975R_e$  for the optimal distance between nearest neighbors in the case of interaction between nearest neighbors, where  $R_e$  is the distance of the minimum of the pair potential, we obtain

$$A = 6.72 - 0.0044\alpha^2R^2. \quad (24)$$

In addition, the sublimation energy for the Morse potential with a short-range interaction in a bulk icosahedral system is

$$\epsilon_{sub} = 6 - 0.00378\alpha^2R^2. \quad (25)$$

For the bulk fcc crystal, these values depend exponentially on the parameter  $\alpha a$ , so that one can use  $\epsilon_{sub} = 6$ , and  $A = 6 \cdot 2^{1/3} = 7.56$  for a short-range interaction potential.

Thus, we have parameters of formula (2) for bulk systems with fcc and icosahedral structures and Morse interactions between atoms. This allows us to determine the optimal form of the fcc structure depending on the parameter  $\alpha$ , and also to find the values  $\alpha_*$  at which the total binding energies for the fcc and icosahedral structures are equal. Now we find a cluster size  $n_*$  at which the binding energies of the fcc and icosahedral clusters become the same. This is

$$n_* = \left( \frac{A_{fcc} - A_{ico}}{\epsilon_{fcc} - \epsilon_{ico}} \right)^3. \quad (26)$$

Here  $\epsilon_{fcc}$  and  $\epsilon_{ico}$  are values of the parameter  $\epsilon_{sub}$  in formula (2) for the fcc and icosahedral structure, respectively, and  $A_{fcc}$  and  $A_{ico}$  are the specific surface energies of these structures. Values of the parameter  $n_*$  as a function of  $\alpha R_e$  are given in Table IV. For large  $\alpha R_e$  this size is determined by formulas (24)–(26):

$$n_* = \left( \frac{235}{\alpha^2 R_e^2} + 1.2 \right)^3. \quad (27)$$

Values of  $n_*$  obtained on the basis of this formula are given in Table IV in parentheses. But strictly we cannot use this formula because it is valid for bulk systems, while the resultant cluster sizes are not large. Indeed, we assume the surface energy to be determined by the interaction of surface atoms that are not edge or vertex atoms. This can be valid only for  $n > 100$ . Indeed, calculations for a short-range interaction of atoms<sup>7</sup> show that the competition of the fcc and icosahedral cluster structures occurs in the range of cluster sizes  $n = 150$ – $500$  for systems with only nearest-neighbor interactions. These results for large values of the Morse parameter  $\alpha R_e$  mark only a tendency in the competition of the struc-

tures. Nevertheless, from this we infer that the competition range has a strong dependence on the contribution of the long-range part of the interaction potential.

#### IV. ENERGETICS OF LARGE MORSE CLUSTERS

We consider a cluster as a system of a finite number of bound atoms. Then the total binding energy of cluster atoms is

$$E = -\frac{1}{2} \sum_{i,k} U(r_{ik}), \quad (28)$$

where  $r_{ik}$  is the distance between the  $k$ th and  $i$ th atoms, and the sum is taken over all the cluster atoms. If we deal with a cluster, this sum has an irregular component, so that the specific cluster energy  $E/n$  as a function of  $n$ , the number of cluster atoms, has local maxima at magic numbers of cluster atoms. In order to take into account the irregular part of the cluster energy for large Morse clusters, we use both numerical and analytical methods. First we use a numerical program, which allows us to determine the distances between each pair of cluster atoms  $r_{ik}$  for the fcc and icosahedral structures in the range of sizes  $n=561-923$ . Second, we account for the cluster "irregularity" associated with interactions between nearest neighbors. In an icosahedral cluster, there are two nearest-neighbor distances, which we denote as  $R$ , the distance between neighbors in adjacent layers, and as  $R_0$ , the distance between neighbors in the same layer;  $R=0.951R_0$ . We consider the interaction potential of non-nearest neighbors as a continuous function of  $n$ , while energies associated with bonds between nearest neighbors (and their counterparts in the icosahedral structure) we find exactly. Next, we determine the optimal configuration of the cluster atoms on the basis of nearest-neighbor interactions. Then, including the interactions of non-nearest atoms, one can find the optimal distances between nearest neighbors for the structures identified in the prior step. Thus, we divide the cluster energy into interactions of nearest neighbors, non-nearest neighbors, and strain energy;<sup>1</sup> this method allows us to calculate each of these terms for any given number of atoms. As it is seen, the problem of determining the cluster energy for large clusters is simpler than for small ones.

Thus, using the Morse interaction potential (1), we represent the total binding energy of cluster atoms (28) in the form

$$E = \exp(\alpha R_e) F(\alpha a) - \frac{1}{2} \exp(2\alpha R_e) F(2\alpha a), \quad (29)$$

where

$$F(\alpha a) = \sum_{i,k} \exp(-\alpha r_{ik}), \quad (30)$$

and  $a$  is the distance between nearest atoms (a basis for this cluster), and the sum is taken over all the bonds. Optimizing the cluster energy  $E$  by the standard method,<sup>18</sup> we find the optimal distance  $a$  from the relation

$$\exp(\alpha R_e) = \varphi(\alpha a) = F'(\alpha a)/F'(2\alpha a), \quad (31)$$

so that the optimal binding energy of the cluster is

$$E = \varphi(\alpha a) F(\alpha a) - \frac{1}{2} \varphi^2(\alpha a) F(2\alpha a). \quad (32)$$

Let us divide the sum (30) in parts  $F = F_{nn} + F_{n\bar{n}}$ , so that  $F_{nn}$  is due to the interaction of nearest neighbors and  $F_{n\bar{n}}$  is determined by the interaction of non-nearest neighbors. Then the cluster energy is<sup>1</sup>

$$E = E_{nn} + E_{n\bar{n}} + E_{str}. \quad (33)$$

Here

$$E_{nn} = \exp(\alpha R_e) F_{nn}(\alpha a) - \frac{1}{2} \exp(2\alpha R_e) F_{nn}(2\alpha a); \quad (34)$$

in the same way we define the energy of interaction of non-nearest neighbors,

$$E_{n\bar{n}} = \exp(\alpha R_e) F_{n\bar{n}}(\alpha a) - \frac{1}{2} \exp(2\alpha R_e) F_{n\bar{n}}(2\alpha a). \quad (35)$$

We take the value  $a$  as the optimal basis for a short-range interaction between atoms. The strain energy accounts for variation of the distance between nearest neighbors of a cluster from the optimal value.

First let us consider the case of a short-range interaction, with only nearest-neighbor interactions taken into account. Then for a fcc cluster we have

$$F_{nn}(a) = K \exp(-\alpha a), \quad F_{n\bar{n}} = 0, \quad (36)$$

where  $K$  is a number of bonds between nearest neighbors of the cluster. This number of bonds reflects the optimal configuration of cluster atoms for a given number of atoms. Below we use these values from Ref. 16. Thus, we have  $F'_{nn} = -F_{nn}$ , so that the energy optimization (6) gives  $\varphi(\alpha a) = \exp(-\alpha a)$ , and  $a = R_e$  for nearest neighbors. Then

$$E = K, \quad (37)$$

and the energy of interaction of non-nearest neighbors, as well as the strain energy  $E_{str}$ , are equal to zero.

Denoting by  $X$  the number of bonds between an atom and its nearest neighbors in adjacent layers of an icosahedral cluster, with bond length  $R$ , and by  $Y$  the number of bonds to atoms in the same layer, with bond length  $R_0$ , we have

$$F_{nn} = X \exp(-\alpha R) + Y \exp(-\alpha R_0). \quad (38)$$

Then, from optimization of the binding energy of cluster atoms, we determine the optimal distance between nearest neighbors of neighboring atoms.<sup>7,8</sup>

$$R = R_e [1 - 0.047Y/(0.904X + Y)]. \quad (39)$$

This leads to the following expression for the total energy of an icosahedral Morse cluster, if we restrict it to the interaction between nearest neighbors only:<sup>7,8</sup>

$$E = X + Y - 0.0024\alpha^2 XY/(0.904X + Y). \quad (40)$$

The equality of the binding energies for the icosahedral and fcc structures occurs at a "critical" value of the Morse range parameter:

$$\alpha_* = 20.4 \cdot \sqrt{(X + Y - K)(0.904X + Y)/(XY)}. \quad (41)$$

Table VIII gives the results of a comparison of cluster parameters for numbers of atoms that correspond to icosahedral structures with filled layers. Table IX contains these parameters for numbers of cluster atoms when ten triangles of the surface layer of an icosahedral cluster are filled. In these tables, values of the parameter  $\alpha_* R_e$  are given that describe the intersection of structure energies in accordance

TABLE VIII. Structures: here  $m$  is the number of filled layers for the icosahedral cluster, and  $n$  is the number of atoms in the cluster. In this and the two following tables,  $X$  is the number of bonds in the icosahedral cluster between nearest neighbors of adjacent layers,  $Y$  is the number of bonds in the icosahedral cluster between nearest neighbors of the same layer, and  $K$  is the number of bonds between nearest neighbors in the fcc cluster.

$m$	$n$	$X$	$Y$	$K$	$\alpha_* R_e$
3	147	276	420	668	8.21
4	309	648	900	1507	6.60
5	561	1260	1650	2844	6.07
6	923	2172	2730	4809	5.54
7	1415	3444	4200	7527	4.96
8	2057	5136	6120	11 118	4.44

with formula (41). The comparison reveals the range of  $\alpha$  where the competition of these structures takes place.

Now let us account for the interaction of non-nearest neighbors as a perturbation, i.e., let us construct a perturbation theory for the Morse potential where the small parameter is  $\Delta = F_{\text{nnn}}(\alpha R_e)/F_{\text{nn}}(\alpha R_e)$ . In any case, this perturbation theory is valid for  $\alpha > 4$ , and Table X gives values this small parameter for fcc ( $\Delta_{\text{fcc}}$ ) and icosahedral ( $\Delta_{\text{ico}}$ ) clusters. In addition, Table X contains the parameter  $\gamma = -d \ln F_{\text{nnn}}(\alpha R_e)/d \ln(\alpha R_e)$ . Since  $1/\gamma$  is a dimensionless parameter that reflects how the distance between cluster atoms affects the value of the three-body strain interaction  $F_{\text{str}}$ , we have  $\gamma > 1$ . For this reason, we can neglect the second term in formula (35) compared to the first one. Indeed, the value  $\exp(\alpha R_e) F_{\text{nnn}}(2\alpha R_e)/F_{\text{nnn}}(\alpha R_e)$  is 0.11 for  $\alpha R_e = 4$ , 0.074 for  $\alpha R_e = 5$ , and 0.054 for  $\alpha R_e = 6$  in the range of cluster sizes  $n = 561-923$ .

Thus, within the framework of our perturbation theory, we have for the binding energy of atoms of fcc clusters,

$$E = 2K \exp[\alpha(R_e - a)] - K \exp[2\alpha(R_e - a)] + 2F_{\text{nnn}}(\alpha a). \quad (42)$$

Optimizing the energy with respect to the distance between nearest neighbors  $a$ , we get, at this distance,

$$\alpha(R_e - a) = \gamma F_{\text{nnn}}(\alpha R_e)/F_{\text{nn}}(\alpha R_e) = \gamma \Delta. \quad (43)$$

From this it follows for terms of formula (34) that

$$E_{\text{nn}} = K, \quad E_{\text{nnn}} = 2KA, \quad E_{\text{str}} = \gamma^2 \Delta^2 K. \quad (44)$$

In the same way, for the icosahedral cluster we have a total binding energy of the cluster atoms,

TABLE IX. Structures: the icosahedral cluster has  $m$  filled layers and ten filled surface triangles above it:  $n$  is the number of cluster atoms. See the caption of Table IX for definitions of  $X$ ,  $Y$ , and  $Z$ .

$m$	$n$	$X$	$Y$	$K$	$\alpha_* R_e$
4	216	442	603	1024	5.74
5	420	928	1203	2094	5.31
6	724	1684	2103	3730	4.93
7	1148	2770	3363	6042	4.89
8	1712	4246	5043	9181	4.32

TABLE X. Parameters of the interaction of non-nearest neighbors in Morse clusters. See the caption of Table IX for definitions of  $X$ ,  $Y$ , and  $Z$ .

$\alpha R_e$	$\gamma_{\text{fcc}}$	$\Delta_{\text{fcc}}$	$\gamma_{\text{ico}}$	$\Delta_{\text{ico}}$
4	1.68	0.21	1.72	0.23
5	1.61	0.11	1.64	0.12
6	1.56	0.061	1.60	0.071
7	1.52	0.036	1.56	0.042
8	1.50	0.021	1.53	0.026
10	1.46	0.0082	1.50	0.010

$$E = X + Y - 0.0024\alpha^2 XY / (0.904X + Y) - (X + 1.106Y)(R' - R)^2 + 2F_{\text{nnn}}(\alpha R) \exp(\alpha R_e), \quad (45)$$

where  $R'$  is given by formula (39), and  $R = R_e [1 - 0.047Y / (0.904X + Y)]$ . Optimizing the cluster binding energy (45) for a given parameter  $\alpha R_e$  with respect to the distance  $R$ , we obtain, for the terms of formula (34),

$$E_{\text{nn}} = X + Y - 0.0024\alpha^2 XY / (0.904X + Y),$$

$$E_{\text{nnn}} = 2F_{\text{nnn}}(\alpha R') \exp(\alpha R_e), \quad (46)$$

$$F_{\text{str}} = \frac{(\gamma\alpha)^2}{X + 1.106Y} F_{\text{nnn}}^2(\alpha R') \exp(2\alpha R_e).$$

It follows from this formula, as with fcc clusters, that  $E_{\text{nnn}}/E_{\text{nn}} \sim \Delta$ ,  $E_{\text{str}}/E_{\text{nn}} \sim \Delta^2$ .

Note that the specific values  $F_{\text{nn}}/n$  and  $F_{\text{nnn}}/n$  at a given  $\alpha R_e$  are smooth functions of the number  $n$  of cluster atoms. For example, in our range of cluster sizes the value  $K$  varies from 2844 for  $n = 561$  to 4809 for  $n = 923$ . Then the value  $K/n$  varies from 5.07 up 5.21, i.e., only within a few percent. The number of bonds between nearest neighbors as a function of  $n$  has jumps at magic numbers of cluster atoms; this becomes especially apparent in a comparison with a smooth function describing this dependence. However, the difference between these functions at magic numbers does not exceed 10, small compared with the total number of bonds. The function  $F_{\text{nnn}}/n$  is a smoother function of the number of atoms because it includes the interaction of non-nearest neighbors. Thus, calculating the cluster binding energy, one can assume the specific energetic parameters to be constant in some range of  $n$ . But it is not correct to assume the same parameters for the analysis of competition of the fcc and icosahedral structures.

Indeed, let us analyze data of Tables VIII and IX. One can see that the numbers of bonds between nearest neighbors are close, so that their relative difference is several percent over a wide range of cluster sizes. Table X shows that the interaction energies of non-nearest neighbors are also close. The results of a comparison of the energy for clusters of different structures are given in Table XI. We give data for the favored structures. The filling layer of the icosahedral cluster can have either an icosahedral or a fcc structure, while its core has the icosahedral structure. Whether the structure of the surface layer is icosahedral or fcc depends sensitively on the number of bonds. The fcc structure of the surface layer of the icosahedral cluster is favored if less than

TABLE XI. Parameters of icosahedral and fcc clusters. The parentheticals ic and fcc mean that a cluster with an icosahedral core has a surface layer of an icosahedral or fcc structure, respectively; c and nc for the fcc cluster mean, respectively, that this cluster has or has no central atom.

$n$	$X$	$Y$	$K$	$\alpha_* R_e$
561	1260(ic)	1650	2844(nc)	7.1
606	1395(fcc)	1740	3093(nc)	6.8
636	1485(fcc)	1800	3255(nc)	6.4
681	1620(fcc)	1890	3490(c)	6.2
688	1592(ic)	1996	3529(c)	6.7
724	1677(ic)	2103	3730(c)	6.7
760	1774(ic)	2210	3934(c)	6.6
817	1916(ic)	2385	4234(c)	6.8
874	2058(ic)	2564	4575(c)	6.5

eight surface triangles of the cluster are filled. For eight or more completed surface triangles, the icosahedral structure of the surface layer is favored.

As for the fcc clusters, the two surface structures compete whether or not the cluster has a central atom. As the number of atoms increases, the favored surface structures alternate. In our range of cluster sizes, with no central atom, the fcc structure tends to be the more stable. In Table IV, the favored structure is marked in parentheses, following  $K$ , the number bonds of the fcc cluster, with the indication (c) or (nc), depending on the presence or absence of a central atom in the fcc structure.

Table XI lists values of the parameter  $\alpha_* R_e$  at which the binding energies of the cluster consisting of a given number of atoms become equal for the most stable configurations of the icosahedral and fcc structures. We use formulas (44) and (46) for the energy of the fcc and icosahedral clusters. Parameters of the icosahedral cluster with a short-range interaction are taken from Refs. 7, 8 and parameters of the most stable configurations of fcc clusters are taken from Ref. 16. Parameters for the long-range interactions, which include the interaction of non-nearest neighbors, are calculated by numerical methods on the basis of formula (30) for the Morse potential. Note that in our range of competition of structures and cluster sizes, i.e., for  $n = 561-923$  and  $\alpha R_e = 6-7$ , the interaction of nearest neighbors gives the main contribution to the total binding energy. This justifies our using the numerical method in which we take the optimal configuration of cluster atoms from that of a short-range interaction. Nevertheless, taking into account the interaction of non-nearest neighbors is important.

Indeed, from the data of Tables VIII, IX, and XI, it follows that the numbers of bonds between nearest neighbors for the fcc and icosahedral clusters are similar, so that though the interaction potential of non-nearest neighbors is small compared to the interaction potential of nearest neighbors in the cluster, this potential can be comparable with the difference between the interaction potentials of nearest neighbors of the two structures. Indeed, one can see from Tables VIII, IX, and XI that the difference  $X+Y-K$  that is inserted in formula (42) is several percent of  $X+Y$ . This is the same order of magnitude as the interaction potential of non-nearest neighbors in the competitive region of range parameters,

$\alpha R_e = 6-7$  (see Table X). For the icosahedral structure, the interaction potential of non-nearest neighbors exceeds that of the fcc structure, so that this interaction increases the parameter  $\alpha_* R_e$  of the intersection of structure energies as compared with the case of a short-range interaction. Note that the strain cluster energy in the intersection range according to formulas (44) and (46) is proportional to  $\Delta^2$  and thus is not essential for this consideration.

The value  $X+Y-K$  is sensitive to the cluster structure. It has maxima at magic numbers of the icosahedral cluster and minima at magic numbers of the fcc cluster. Hence, in a range of cluster sizes, which includes magic numbers, the value  $\alpha_* R_e$  is an irregular function of  $n$ , the number of cluster atoms. The interaction of non-nearest neighbors makes this function smoother because this interaction is not sensitive to magic numbers.

The Lennard-Jones atom-atom potential yields clusters with properties very similar to those of a cluster whose atoms interact via a Morse potential with  $\alpha R_e = 6$ . Thus, from the foregoing analysis, it is natural to suppose that the icosahedral and fcc structures of Lennard-Jones clusters become competitive at  $n \geq 1000$ , in accordance with Ref. 11.

## V. CONCLUSION

Thus, we conclude that it is convenient to use the Morse parameter  $\alpha_* R_e$  to characterize the range where two structures compete, i.e., at which the energies of clusters of a given size are approximately equal for optimal configurations of clusters of the fcc and icosahedral structures.<sup>13</sup> We have carried out numerical calculations for the energies of clusters consisting of numbers of atoms  $n = 561-923$ , which correspond to filling of the sixth layer of the icosahedral cluster. It follows from these calculations and the above analysis that the parameter value at which the energies are approximately equal is determined by the interactions of both nearest and non-nearest neighbors in clusters. The parameter  $\alpha_* R_e$  for these cluster sizes lies in the range 6-7 and is a nonmonotonic function of the number of atoms. In this range of  $\alpha R_e$  the main contribution to the atomic binding energies of structures considered here is the interaction of nearest neighbors, while interaction of non-nearest neighbors is several percent of this. Nevertheless, because the numbers of bonds between nearest neighbors are similar for optimal configurations of fcc and icosahedral clusters, taking into account the interaction of non-nearest neighbors is essential for determining the parameter  $\alpha_* R_e$  at which the energies of different structures coincide. Interactions of non-nearest neighbors increase  $\alpha_* R_e$  and make this a smoother function of the number of cluster atoms.

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