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The energetics of large Lennard-Jones clusters: transition to the hexagonal close-packed structure

N.V. Krainyukova[a]

Institute for Low Temperature Physics and Engineering NASU, 47 Lenin ave., Kharkov 61103, Ukraine

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Abstract. The energetics of large multiply twined particles (MTPs) such as decahedra with fivefold symmetry, face-centred cubic (fcc) and hexagonal close-packed (hcp) clusters in size from 2000 to ∼45000 atoms was numerically analysed. Clusters were relaxed freely under the Lennard-Jones pair potential to the energy minimum. The essential extension of size compared to previous studies and the additional shape-optimisation of hcp and fcc clusters as well as truncated decahedra appears to be of high importance in the potential energy analysis. The best-optimised decahedra were confirmed to be the most favourable structure from 2000 to $\sim 10^5$ atoms. Only in the short size interval, above $N \sim 10000$ atoms, the best-optimised fcc clusters and simplest Marks' decahedra could alternate, while above $N \sim 14000$ atoms does the shape-optimised hcp structure be proved to become more favourable for single crystal particles compared to the best-optimised fcc structure. Depending on shapes and sizes, decahedra and hcp clusters can alternate in the wide size interval above $N \sim 14000$ atoms and presumably form the mixed abundances of clusters belonging to the both symmetries. Finally, the upper limit for stable MTPs was estimated to be about $N \sim 10^5$ atoms, while above only the hcp clusters are the most favourable.

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1 Introduction

For over 20 years the problem of size-dependent structural transformations between clusters with different symmetries including multiply-twined particles (MTPs) has been of high scientific interest and solved in a framework of the elasticity theory [1,2] as well as by structural relaxation [3–10] and molecular dynamics [11–14] methods for different structural models and applied potentials. Such MTPs as icosahedra (ico) and decahedra (dec) with five-fold symmetry appear due to their minimal surface energy reached in these clusters compared with single crystal formations. Numerous facts of the MTPs observation in gas expansion experiments [14–23] and in the growth on substrate [24–26] at relatively high supersaturations are reported. They can be expected in impurity-helium solids [27–29] and for substances formed in porous matrixes [30–37]. But for larger sizes, deformations around five-fold symmetry axes make these structures unfavourable.

In the previous work [38] we analysed one of the fundamental aspects of size-dependent transformations, i.e. their application to the well-known 'Rare gas solids problem' [3,39,40], which can be formulated as a contradiction between the theoretical prediction of the hcp structure in the heavier noble gas crystals and the dominant experimental observations of fcc-like structures. We showed, applying the partly optimised Marks' decahedra and the newly included hcp clusters, that MTPs, which comprise twined fcc fragments, at very large sizes do transform into the hcp structure typical of the bulk. Here we present the extension of the previous work applying the better optimised hcp clusters. These clusters are compared with different decahedra (including their forms lowest in the potential energy) and we also analyse the role of cluster shapes formed during the growth process in the real experimental observations.

2 Structural models

The most favourable icosahedra (in their surface energy) were shown in several studies [5,9,38] to lose their energetic prevalence in favour of decahedra at cluster sizes $N \sim 2000$ atoms. Hence, here we analyse clusters with larger sizes. In view of the importance of minimal surface energies for size-dependent transformations, it was natural first to calculate energies for spherical clusters cut from icosahedra, decahedra, hexagonal and cubic clusters. It was previously shown [37], that such spheres cut in an arbitrary way are less favourable in potential energy than perfectly shaped clusters. This fact was ascribed to the

[a] e-mail: krainyukova@ilt.kharkov.ua

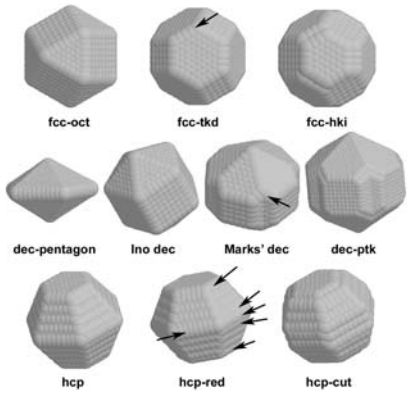

Fig. 1. Structural models for clusters. The upper row presents different forms of fcc clusters: (cub)octahedra (fcc-oct), fcc-tkd and fcc-hki. In the second row decahedra are shown. The bottom row demonstrates the evolution of hcp clusters towards their best-optimised form hcp-cut. Arrows indicate edges removed in the most favourable form. The shape-dependent potential energies decrease from left to right for all structural types.

reduction of the number of nearest neighbours for surface atoms in spherical clusters compared with perfect shapes with completed shells. Only cuboctahedra were found to be the clusters, which lose their advantage in competition with spherical forms cut arbitrary. Nevertheless, as we will see in the further analysis, certain atoms precisely cut from edges and vertices give rise to essential energetic advantages in the procedure of the cluster shape optimisation. The resulting clusters are more spherical!

The cuboctahedra (oct) (Fig. 1, the upper row) were previously proven [5,6] not to be the most favourable form of fcc clusters. Two other shapes of fcc particles termed by authors [5] as tkd (tetrakaidecahedra) and hki (hexakaiicosahedra) were found to have lower potential energies, the lowest for the hki. The tkd clusters are truncated (cub)octahedra with square and hexagonal edges of equal length. To produce the hki, we have to remove one row of atoms at all (111)/(111) edges of the tkd. Decahedra were first introduced in the pentagonal form [41] (Fig. 1, the second row). Later, they were improved by Ino [42] and Marks [1] decreasing, step by step, their potential energies. In every step the removed atoms smoothed sharp edges. In decahedra re-entrant additional lateral facets (111) (the most favourable faces) of different depths were suggested by Marks; it is worth noting that by means of such a procedure we reduce stresses owed to deformations arising around the five-fold symmetry axes. The Marks' dec are described by an integer triplet $[m, n, s]$, m and n the numbers of atoms on the sides of the rectangular (100) faces, $s + 1$ is the number of atoms on edges between lateral and top/bottom (111) faces. Raoult's [5] and Cleveland's [9] calculations showed that the square (100) faces with $m = n$ atoms are the best choice. The best form of dec termed as ptk (pentakaitetrakontahedra [5]) was produced by removing one row of $s + 1$ atoms from 20 (110) facets. In our previous work [38] multishell hexagonal clusters (truncated bipyramid [43]) seem to be first included in the energy analysis. The improvements in the potential energies are reached in a similar way as for other structures. The first step was to remove the outermost basal planes that increased the ratio between numbers of atoms on the most favourable basal planes (001) and lateral hexagonal (111) faces (Fig. 1, the hcp-red means the reduced hcp). The next, much more important improvement suggested in the present work was made by means of removing all edges around basal faces and central edges in the hexagonal truncated bipyramid (one row along three central edges and three rows along the other three edges, as shown in the bottom row in Fig. 1 — transforming the hcp-red into the hcp-cut). In our further analysis we consider only the more favourable forms: the fcc-tkd, the fcc-hki (both centred), Marks' and the ptk decahedra, as well as hcp clusters in their multishell (hcp) and best shape-optimised forms (hcp-cut).

3 Energy calculations

Clusters were relaxed freely under the Lennard-Jones pair potential to the energy minimum applying the cut-off radius $5r_0$ (r_0 is the nearest neighbour distance) in the same way as it was made previously [3,4,6,38]. All calculated energy values are expressed via units of the binding (positive) energy of an atomic pair. Raoult et al. [5] showed that calculated potential energies (per atom) exhibit dependence on a clusters size, which is very close to linear, if they are expressed as a function of $N^{-1/3}$. We used this observation in order to compare discrete energies calculated for different structures with the energy of the best-optimised hcp (hcp-cut) clusters, which was expected [38] to be the most favourable formation at $N \to \infty$. Thus, we compare discrete values of potential energies calculated for the fcc-tkd, the fcc-hki, Marks' and ptk decahedra as well as hcp clusters with linearly interpolated potential energies (per atom) of the hcp-cut termed further as $E_{\min}$. In Figure 2a we show $E_{\min}$ as a function of the cluster size; $E_{\min}$ tends to the bulk meaning –8.610 at $N \to \infty$. Calculations of relative energies $(E_{\min}–E)N^{1/3}/E_{\min}$ vs. $N^{-1/3}$ are illustrated in Figure 2b. The relative energies presentation is equivalent to the expression of relative energies approximately per unit surface area. Positive values of this ratio correspond to structures, which are less favourable than the hcp-cut and vice versa. Over the whole size interval under study the hcp-cut are certainly much more favourable than multishell hcp clusters and partly optimised fcc-tkd. The most favourable fcc clusters termed hki appear to be able to compete successfully only with simplest Marks' decahedra with $s = 2$ in a very short size interval from $N \sim 10000$ atoms to $N \sim 14000$ atoms. The competition of two single crystals: one is the currently accepted best-optimised form of the fcc structure termed hki [5] and the other is the hcp-cut clusters introduced in this work, exhibits the prevalence of the hcp for sizes larger than $N \sim 14000$ atoms. Marks' decahedra with $s = 2$ lose their advantage as compared with the hcp-cut at $N \sim 11000$ atoms, with $s = 3$ at $N \sim 27000$ atoms and with $s = 4$ at $N \sim 47000$ atoms. But decahedra in

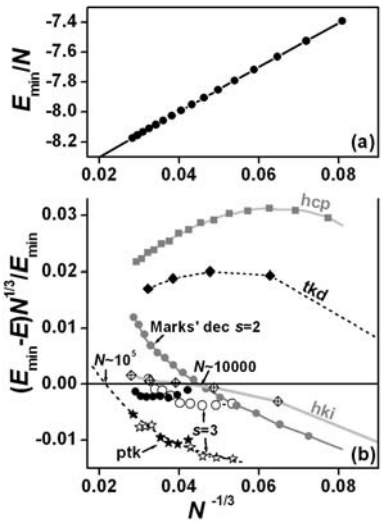

Fig. 2. Size dependence of the potential energy $E_{\min}$ (per atom) for the best form of hcp clusters (hcp-cut) (a). Relative differences in potential energies E for several types of clusters: multishell hcp clusters (squares), fcc-tkd (solid diamonds), fcc-hki (diamonds with crosses), Marks' dec (circles) and ptk decahedra (stars) with respect to the best-optimised hcp structure (b). The dec with even and odd s are shown by solid and open signs respectively to be visually separated from each other.

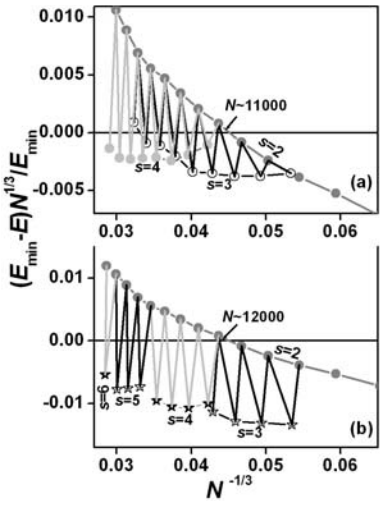

Fig. 3. Shape and growth induced oscillations between structures. Marks' decahedra 'oscillate' between different s during the growth process (a). The same for simplest Marks' decahedra and ptk (b).

their best-optimised form (the ptk) accordingly to our estimation can successfully compete with single crystals and preserve their energetic prevalence far above the largest size considered in this work.

Basically, the prediction of the single crystal structure prevalence comparatively with MTPs made by Raoult et al. [5] when cluster sizes attain $\sim 10^5$ atoms is very close to our estimation of the upper limit of the energetically stable five-fold symmetry particles, but the single cluster structure in our case is found to be hcp in line with the calculations made [39,40] for bulk crystals and in contrast with expected earlier the fcc-hki.

4 Shape and growth induced oscillations between structures

The general picture would be incomplete if we disregarded the real experimental conditions imposing numerous corrections to the ideal sequences of the most favourable structures with 'magic' numbers inherent in the certain size intervals. Indeed, instead of the discrete cluster sizes corresponding to the most favourable structures with completed facets in reality we should always expect some deviations [44] or intermediate sizes rather than the exact coincidence with theoretical models. This argument is of increasing relevance in view of the general character of the shape optimisation procedure. We cut the sharp edges and vertices one by one to reach the optimum. But in the real growth processes the same atoms could be added that result in possible jumps or oscillations between structures belonging to different structural types or even symmetries if atoms in initial clusters are in sufficiently mobile states. We should emphasize that oscillations in our context do not mean the transformations between clusters, which already form. We presume that initially highly mobile clusters before crystallization have different numbers of atoms, i.e. not exactly corresponding to the best configurations, and these numbers deviate in real experiments. These deviations may be the reason for incomplete intermediate shells that result in more favourable (e.g.) hcp-cut for some intermediate sizes. There are plenty of possible schemes. Let us consider at least two simple examples.

Marks' decahedra with different depths s of re-entrant (111) facets are more or less favourable depending on cluster sizes [6] (see also Fig. 2). But in the real growth process the new shell formation can start precisely inside such re-entrant regions because the deepest atoms have in this case the maximal number of nearest neighbours ($NN = 10$) and hence the lowest potential energies comparatively with all other surface atoms. Thus, during the crystallization, which starts in clusters with deviated N, observed structures could fluctuate between different s. This results in alternations not only between different decahedra types but also can cause the appearance of a small fraction of hcp-cut clusters above $N \sim 11000$ atoms (it corresponds to positive values of the ratio $(E_{\min} - E)N^{1/3}/E_{\min}$ in Fig. 3). At growing initial sizes N this fraction can increase due to larger oscillations and also owing to the reduced advantage of decahedra.

A very similar situation can be realized if we compare the best form of decahedra ptk with simplest Marks' decahedra. Edges and vertices removed in the shape optimisation procedure can appear again in the further shells. The resulting oscillations are larger as compared with the previous case and can also induce a noticeable fraction of hcp-cut clusters starting from $N \sim 12000$ atoms. But up to very large sizes $\sim 10^5$ atoms, ptk decahedra with completed shells are obviously dominant because their potential energies are lowest.

Here we should emphasize that we do not expect structural transformations between different symmetries because of the huge barriers separating such structures [38]; presumed oscillations appear exclusively due to slightly

deviated initial sizes, and for this reason structures obtained during crystallization belong to different symmetries.

Our findings strongly correlate with observations of the large population of hcp clusters in the size interval 20000–10^5 atoms by means of the electron diffraction method in gas expansion experiments [17,18], although such clusters were not dominant. In view of the analysis suggested in this work, hcp clusters should be mixed with decahedra, which prevail in this size interval.

5 Conclusions

Compared with previous studies, in this work we introduced the best form of hcp clusters (hcp-cut) and compared them with highly shape-optimised fcc particles and decahedra. We showed that in the competition between single crystals fcc and hcp, the optimised fcc-hki could prevail only below $N \sim 14000$ in cluster sizes. But in this range decahedra are nearly absolutely dominant. Above $N \sim 14000$ atoms the optimised hcp-cut become more favourable with respect to all known fcc forms.

MTPs can be considered as a compromise between fcc and hcp because they comprise fcc fragments jointed together through twin boundaries and all atoms along twins have the hcp-like surrounding. Comparing potential energies of decahedra and the best form of hcp (hcp-cut) we see that Marks' decahedra lose their advantage depending on the depth of re-entrant (111) facets at $N \sim 11000$ for $s = 2$, at $N \sim 27000$ for $s = 3$ and at $N \sim 47000$ atoms for $s = 4$ and practically these types of perfectly shaped decahedra can hardly be favourable above $N \sim 50000$ atoms. The ptk decahedra, which are essentially better optimised, can preserve their advantage as compared with single crystals up to $N \sim 10^5$ atoms in line with the previous estimation [5]. We have found that the single crystal structure hcp (in its hcp-cut form), expected at very large sizes, strictly corresponds to the well known theoretical prediction [39,40] made for rare gas solids long ago. We expect that different potentials as well as an application of the other cut-off radiuses can only slightly shift the size-dependent transformation points (see also [38]), because these points are not imposed by the absolute energetic values but are rather determined by the relative energies. Thus, we see again [38] that the 'Rare Gas Solids problem' considered in conjunction with size-dependent structures can eliminate the previous contradiction, i.e. MTPs comprising fcc fragments appear at smaller sizes while the hcp is the most favourable structure at large sizes and in the bulk in complete agreement with the theory.

Real experimental conditions inherent in different growth processes should impose 'oscillations' between structures or even symmetries. It could explain the essential population of hcp-like clusters (which nevertheless were not dominant) observed in gas expansion experiments by two experimental groups [17,18] independently. Evidently in the size interval ∼17000–10^5 atoms decahedra should be mixed with hexagonal clusters in their best-optimised forms and the fraction of the latter has to increase gradually with the average cluster size.

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