Structure of binary clusters: are icosahedra relevant?

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Abstract

We investigate the structure of 13-particle clusters in binary alloys for various size ratios and different concentrations via MD simulation. Our goal is to predict which systems are likely to form local icosahedral structures when rapidly supercooled from the melt. We calculate the energy spectrum of the minimal energy structures, and characterize all detected minima from both their relative probability and from a structural point of view. We identify regions in our parameter space where the icosahedral structure is dominant (like in the corresponding monoatomic case), regions where the icosahedral structure disappears and other where icosahedral structures are present but not dominant. Finally, we compare our results with simulations reported in literature and performed on extended binary systems with various size ratios and at different concentration.
I. INTRODUCTION

Over the last decade, chemists and solid state physicists have been greatly interested in the platonic solid with the highest symmetry: the icosahedron. Chemists became interested in icosahedra because several clusters have been found to be icosahedral or poly-icosahedral. In particular, the recent synthesis and structural determinations of metal carbonyl clusters resulted in a variety of icosahedral clusters containing transition metals and main group elements [1]. Solid state physicists believed until recently that icosahedral symmetry played no role in extended structures because it is not compatible with periodic arrangement of structural units (i.e. with crystalline order). It is now known that icosahedral symmetry is compatible with quasiperiodic translational order, and states of matter arranged in such a way have been found (i.e. quasicrystals [2]). Moreover, icosahedral structures are suggested to be important in disordered systems, like supercooled liquids and glasses [3]. The presence of icosahedra in simple supercooled liquid and glasses was revealed by means of computer simulations: from the pioneeristic work of Steinhard, Nelson and Ronchetti [4] up to the most recent works [5], there is evidence in literature that it is so for monoatomic supercooled liquids and glasses interacting via Lennard-Jones (LJ) and via a variety of different metallic potentials [6]. So far however studies of LJ binary systems yield contrasting results [7]. The study of icosahedral clusters is therefore important both in itself and because it can give hints on the presence of such structures in disordered systems and on the nucleation of extended icosahedral quasicrystals. Computer simulation performed by Honeycutt et al. [8] on homogeneous LJ systems showed that icosahedrally symmetric clusters are the lowest in energy up to a size of 5000 atoms. A similar study in binary systems would be interesting, but unfortunately it is difficult because the parameter space to be investigated is far more complex. Infact in the case of monoatomic species only the interaction potential and the cluster size (i.e. the number of particles) have to be specified, while in binary systems the relative abundance of the two species, geometric factors (i.e. size ratios) and parameters relative to the binding energy have to be taken into account. For this reason computational
studies on mixtures are rare and focused on specific aspects, like the study of impurities in clusters [9] or the dynamics of phase separation [10]. To start exploring clusters in a binary system it is therefore necessary to reduce the search space by fixing a few parameters and studying the dependence on the remaining ones. For instance, both the above referred works by Garzon et al. [9] and Clarke et al. [10] keep the geometric parameters fixed and vary the energetics. In the present work we decided to cut the parameter space in an orthogonal direction by fixing the energetic parameters and the size of the cluster, and varying particle size and concentration. We therefore use the same depth of the potential well for both atomic species and for the interaction between unlike particles. For the cluster size we focus on 13-particles clusters, since our aim is to determine the importance of icosahedral structures. We therefore study the geometric structure and energy spectrum of 13-atom clusters for four different atomic size ratios and for all possible relative concentrations. In the next section we present the details of the computational model. In section III we discuss the methods of measurements that we used. The results are presented in section IV, followed by a discussion and a comparison with the literature (section V).

II. THE COMPUTATIONAL MODEL

We studied a system composed of 13 particles belonging to two different species (L and S) and interacting with a LJ isotropic potential. The two species differ because of geometric factors: the radius of L-atoms is larger than the radius of S-atoms. The interaction between S-atoms is characterized by the parameters \( \sigma_{SS} \) and \( \epsilon_{SS} \): the interaction potential is therefore \( V(r) = 4\epsilon_{SS}[(\sigma_{SS}/r)^{12} - (\sigma_{SS}/r)^{6}] \). The potential for the atomic specie L was defined by \( \epsilon_{LL} = \epsilon_{SS} \) and \( \sigma_{LL} = \alpha\sigma_{SS} \): the parameter \( \alpha \) therefore fixes the ratio between the radii of the two species. The interaction between unlike particles was defined by \( \epsilon_{LS} = \epsilon_{SS} = \epsilon_{LL} \) and \( \sigma_{LS} = (\sigma_{LL} + \sigma_{SS})/2 \). The values of \( \sigma_{SS} \) and \( \epsilon_{SS} \) were suited to Argon (this choice does not invalidate the generality of the results, since its only consequence is to fix the energy and length scales). The mass is not a relevant parameter when only structural properties are
of interest, and we therefore used equal masses for the two species (again, we chose Argon mass). In the following all results are given in reduced units with $\epsilon_{SS}$ the unit of energy, $\sigma_{SS}$ the unit of length and $(m\sigma_{SS}^2/48\epsilon_{SS})^{1/2}$ the unit of time.

The only relevant parameter is therefore $\alpha$ which fixes the size ratio between the two species. In the limiting case $\alpha=1$ the system is monoatomic since the parameters for L and S-atoms coincide. We used four different values for $\alpha$: 1.6, 1.4, 1.33 and 1.25. A cluster in such model is further identified by the number $N$ of particles composing it and by the relative concentration of L and S-atoms. We fixed $N=13$ and studied all possible concentrations of $\eta \in \{1, 12\}$, where $\eta$ is the number of S-atoms (the limiting cases $\eta=0$ and $\eta=13$ are equivalent, since they both corresponds to a monoatomic system). Our investigation covers therefore 48 points in parameter space. Our simulation method was the Molecular Dynamics technique in the microcanonical ensemble. We used Verlet algorithm with a time step of 0.01 in our reduced units. Clusters were kept in free boundary conditions, and we checked that no atoms evaporated during the runs (cases in which atoms evaporated were discarded since we were interested only in 13-atoms clusters). For each value of $\alpha$ and $\eta$ we produced a large number of independent realizations using two different algorithms which yielded similar results. The first procedure consisted in starting (at equilibrium) from a liquid monoatomic cluster composed of large particles. Then $\eta$ large atoms were randomly substituted by small atoms, and the obtained cluster was allowed to relax for 10000 time steps so as to equilibrate the new system. The cluster was then quenched into a minimum of its potential energy hypersurface. The whole process was repeated for a reasonably large number of times (typically 1000 times). We collected the final configurations and examined them by studying the resulting energy spectrum and the geometric configurations corresponding to the most relevant final states. The second procedure consisted in evolving for a very long time (typically 20 million steps) a liquid cluster formed by $\eta$ small particles and $13 - \eta$ large particles, taking snapshots every 10000 steps. The temperature is high enough that two configurations separated by 10000 time-steps are statistically independent from each other. Each of the snapshots was then relaxed until the cluster reached the local minimum
in potential energy, resulting in 1000 to 2000 independent configurations, which were then studied. Since we use a microcanonic Molecular Dynamics, by using the second procedure all the snapshots (for a given concentration) have the same total energy, while in the former case each initial configuration has different total energy. In spite of the different procedures, the two processes yield equivalent results: in particular the energies of the quenched clusters found with the two methods are the same, suggesting that the configurations we obtain do not depend on the particular history of the sample.

To reach the minimum energy configuration we used a steepest descent minimization: the kinetic energy was quickly stolen so that the cluster fell into the nearest potential energy well without having many chances to perform additional explorations in the configuration space while approaching a local energy minimum. The method corresponds roughly to a cooling rate of $10^{14}$ K/sec. For each of the 48 points in our parameter space we produced at least 2000 configurations. For a set of points a first analysis revealed complex behaviours: in such cases we collected more statistics, producing up to 4000 additional configurations. To avoid that some very rare configurations gain a considerable weight in our statistic, we consider only those minima which appear at least twice in our collection.

III. THE METHODS OF MEASUREMENTS

We were interested in identifying the structures which characterize the quenched clusters from both a structural and an energetic point of view. A first classification can be obtained by looking at the energy distribution of the collection of frozen samples: for each value of $\alpha$ and $\eta$ we study the energy spectrum, i.e. we count the number of different potential energies reached at the end of the quenching process by our samples. There will be a lowest minimum, corresponding to the absolute minimum energy (i.e. the lowest minum in the potential energy surface) and then set of many excited states. If there are significant gaps in the spectrum and moreover different structural properties are detected on either side of the gap, we can say that different phases are present in the system. Here we use the concept of
phase discussed in depth by Honeycutt and Andersen [8]: a phase corresponds to a set of structures of minimum energy (inherent structures). Different phases are characterized by different sets of structures with different properties.

Not all energy minima will be reached with equal probability: we therefore associate to each minimum the corresponding frequency of visits, defined as the ratio between the number of times that a particular value of energy has been reached and the total number of samples produced. Having obtained this information, we can plot the frequencies versus energies: such a plot reveals interesting features of the system under investigation.

We then study the geometric configuration of the quenched clusters. The structural analysis has been performed with various methods presented in literature: Voronoi polyhedra, Common Neighbours Analisys (CNA) [8] and Steinhardt’s invariants [4]. These (and other) methods for investigating the presence of icosahedral structures were recently described in detail in a paper [7] where their validity was investigated. The technique of the Voronoi polyhedron is our main instrument. Given a cluster, our algorithm identifies the central atom(s) (as the atom(s) with the highest number of first neighbors) and then tries to determine the corresponding polyhedron(s). Polyhedra classification is based on the number of faces and on the number of edges of every face. A typical polyhedron is expressed with a set of 5 indexes indicating the number of faces with 3,4,5,6,7 edges. (The probability to find faces with more than 7 edges is negligible). In this way we characterize the structure of every cluster: for instance the polyhedron for a particle at the center of a perfect icosahedral arrangement is the dual of the icosahedron, i.e. a dodecaedron (12 faces, each of them with 5 edges): the set is therefore (0,0,12,0,0). In a few pathological cases the program was not able to construct the polyhedron: the cause of the failures is essentialy due to the fact that for some clusters the central atom has too few neighbors to allow our code to work (i.e. the cluster is very elongated).

As second tool we used the CNA diagram in the new formulation recently proposed by Jónsson [12]. We classify every cluster by looking at the CNA diagrams which involve the central atom. This technique allows to discriminate between different configurations which
exhibit the same Voronoi polyhedron (such cases are mostly due to different arrangements of particles on a second shell). This method also permits to distinguish between configurations which are geometrically similar but differ for the relative placement of L and S-atoms. Finally, we still needed to distinguish between clusters which were classified as icosahedral by the above methods, but which had a different degree of distortion. We found the use of the invariants proposed by Steinhardt et al. [4] very effective for such measure. A number of clusters were also examined visually with the help of computer graphics programs [12,13]. The number of configurations inspected in such way is obviously limited when compared to the great number of clusters produced: we looked mostly at the configurations identified as interesting by the previous analysis. We found the results of visual inspection very useful for reaching a better understanding of the phenomenology.

IV. RESULTS

We now present the results of our investigation. We divide the presentation in two steps: first we discuss the energetics of the clusters by studying the number of minima with respect to the energy (energy spectrum) and the number of visits of every minima (frequency of visits). Later we will examine the corresponding structures to understand in more detail the behavior of the systems.

A. Energetics

The energy of the clusters is first examined by looking at the energy spectrum as a function of $\eta$. Fig. [1] shows the spectra for the various size ratios ($\alpha=1.25$ in fig.1A, $\alpha=1.33$ in fig.1B, $\alpha=1.4$ in fig.1C, $\alpha=1.6$ in fig.1D). In each of the figures an horizontal segment shows an energy level. On the x-axis we have the different values of the concentration $\eta$: the number of small atoms grows when moving from left to right. We show a window having a height of $0.3\epsilon$, which is large enough to give a complete representation of the energy distribution above the absolute minimum. The heigh of such window is comparable to that
reported by Honeycutt and Andersen on the simulation performed on monoatomic 13 atom cluster [8]. In some cases this range includes the region where evaporation begins to occur.

For each energy level \( E \) and for each concentration \( \eta \) we then study the frequency \( \phi_\eta(E) \), defined as the number of times we find a configuration having an energy between \( E \) and \( E + \delta E \) over the total number of configurations produced. Although \( \delta E \) is small (0.01\( \epsilon \)) it gives a coarse graining effect because of the even smaller energy differences among the minima.

Frequencies \( \phi_\eta(E) \) versus \( E \) are reported in Fig. 2, where again the letters A, B, C and D refer to the ratios \( \alpha = 1.25, 1.33, 1.4 \) and 1.6 respectively. In each figure we plot a line for each value of \( \eta \), and in order to increase readability we perform a shift proportional to \( \eta \) of the value \( \phi_\eta(E) \) (i.e. the lowest line corresponds to \( \eta = 1 \), the next lowest to \( \eta = 2 \) and so on). The highest peak at an energy \( E \) indicates that the most likely configuration (for that particular values \( \alpha \) and \( \eta \)) has energy \( E \). If only energetics was important, the most visited configuration should always be the one at the lowest energy. We will see that this is not always the case, showing that also entropy plays an important role in determining the most relevant state(s).

Having described the structure of the figures, we now pass to their interpretation and discussion. The most striking feature of the spectra is the existence of an energy gap which is most evident for \( \alpha = 1.25 \): it is however smaller than for a monatomic system [13]. Below the gap the states are discrete, while above it a continuum of states exists, showing the signature of a liquid-like state. The continuum is not completely sampled by our simulations. At \( \alpha = 1.25 \) for high values of \( \eta \) all the states fall in the continuum, while for values of \( \eta \) smaller than 8 isolated states are present above the gap but below the continuum. The number of such isolated states grows as \( \eta \) decreases: they tend to populate the gap for small values of \( \eta \).

The lowest bound of the continuum seems to follow a parabolic-like behavior as a function of \( \eta \), reaching a minimum for \( \eta \) between 5 and 7. Also the lowest energy state follows a similar behavior. For \( \alpha = 1.33 \) a similar behavior is observed, with a few differences. The gap tends to close for low \( \eta \)'s due to two effects: the lowest energy moves toward higher energies and the number of discrete states below the continuum grows. At \( \alpha = 1.40 \) such
tendency is enhanced, leading to a qualitative transition: it is not clear any more that a gap exists when $\eta \leq 5$. At $\alpha=1.60$ such trend is confirmed: the gap disappears already at $\eta=7$. We will further discuss the gap in a later section, after having identified the structures responsible for this behavior. Figure 3 shows the value of the lowest energy as a function of $\eta$ for the various values of $\alpha$. Of course the minimum energy has the same value for all $\alpha$’s when $\eta=0$ or $\eta=13$, since these cases describe the same system: a monoatomic cluster. The energy always decreases when including an impurity of type 1 ($\eta=12$) and increases if the impurity is a small enough particle ($\eta = 1, \alpha \leq 1.33$). As we already mentioned, the energy behavior is parabolic-like for $\alpha=1.25$, with a minimum for $\eta=7$. As $\alpha$ reaches the intermediate values ($\alpha=1.33, \alpha=1.4$) the shape does not change: the minimum remains at $\eta=7$ but the energy of the minima increases in a more pronounced way on the left side of the curve (i.e. in the region where the concentration of small atoms is smaller). At $\alpha=1.6$ however the situation is quite different: the curve presents two different minima respectively at $\eta=4$ and $\eta=9$, implying the existence of two different mechanisms. Again, before discussing further this point, we will need to perform some structural examination.

The examination of frequency of visits shown in figure 2 enriches the above observations. For $\alpha=1.25$ we can see that the energy states below the gap are the most frequented. Above the gap instead the states in the continuum follow a rather flat distribution, except for $\eta=1$ and 2 where the lowest isolated states above the gap but below the continuum show a significant occupancy. For $\alpha=1.33$ the scenario is similar, with a notable difference: for $\eta \leq 3$ the states at the lowest energies (below the gap) are not the most visited ones: rather, the most frequented states are the lowest in energy above the gap. The same is true for $\alpha=1.4$ and $\eta \leq 5$. At this size ratio it is also evident from figure 2C that the gap disappears for the lowest half of the range. The case $\alpha=1.6$ shows an interesting behavior. At high values of $\eta$ the scenario is similar to that of the previous cases: the dominant peak is at the lowest energy. When $\eta$ decreases the height of the dominant peak decreases and the gap shrinks. Above the gap a continuum of states has a rather flat distribution. The gap disappears for $\eta=8$. For $5 \leq \eta \leq 7$ no structure can be observed, as in the low range for $\alpha=1.33$ and
1.4. At $\eta=4$ however a new, different feature appears: a peak develops at the lowest energy. The height of this peak grows when $\eta$ decreases. This time no energy gap separates the high peak from the structures at higher energies. Finally, the case $\eta=1$ is singular: the most frequented states are the two at the lowest energies, where twin peaks are found. The energy of these states is much higher than for $\eta > 1$.

The behaviour of the energy gap is shown in fig. 4. The gap grows with $\eta$, and converges to a similar value for all concentrations when only one L particle is present ($\eta=12$). The presence of a clear gap in a similar monoatomic system is known to be the signature of the presence of icosahedra [14]. The value of the gap for monoatomic systems is $0.219\epsilon$ [15], close to the value we get for $\eta = 12$ for all $\alpha$’s. As we will see later, when discussing the icosahedral structures, this seems also to be the case for binary mixtures.

B. Structural Analysis

Having identified interesting regions and peaks, we analyse the samples to find which structures are responsible for the behavior we described above. Due to the very large number of minima found, it is obviously unfeasable to examine in detail all of the corresponding clusters. We therefore decided to focus our structural analysis on the configurations having a percentage of visits greater than 1.5%. In addition, we arbitrarily decided to examine also a few other configurations which we considered to be potentially interesting (like for instance the lowest energy configurations also in cases where they are not frequently visited). 3-D images of selected configurations helped understanding the structure of selected clusters.

A first indication comes from an analysis with Voronoi polyhedra. Figures 5 (A,B,C and D for $\alpha=1.25$, 1.33, 1.4 and 1.6) shows the percentage of the most relevant polyhedra as a function of $\eta$. To avoid cluttering the figures with too many data, we show here the behavior of two most relevant polyhedra, and collect all the other polyhedra in a common group. We can see that for $\alpha=1.33$ and high $\eta$’s the dominant structure is a 12-faced polyhedron. At about mid-range the presence of such figure starts dropping, and steadily decreases down to a 10%
for $\eta=2$. The growth of the signal of other-than-12-faced polyhedra at low concentrations is mainly due to 10-faced polyhedra: only 11 atoms form the Voronoi cage while the two remaining particles are on the second shell. A such cluster is reported in fig. 3: the signature of its cage is $(0,2,8,0,0)$, meaning that 2 faces have 4 edges, 8 faces are pentagonal and no face has 3, 6 or 7 edges. The scenario is similar for $\eta=1.4$, the difference being that the drop of the 12-faced polyhedron is much sharper, and very few such structures are found in the range $1 \leq \eta \leq 4$. Again, the competing structure is a 10-faced polyhedron which dominates the low-$\eta$ region. The behavior is instead quite different in the two extreme cases: $\alpha=1.25$ and $\alpha=1.6$. In the first case the 12-faced polyhedron is the dominating king over the whole range: other structure comes close to a noticeability edge only for $\eta \leq 2$. Quite the opposite situation is found at $\alpha=1.6$: 12-faced polyhedra survive only for very high $\eta$'s (i.e. for a cluster of S-atoms with a few L impurities). At the other end of the range (i.e. in a cluster of L-atoms with few S impurities) the dominating structure is the 9-faced polyhedron. The 3D graphical representation of such polyhedron for the case $\eta=2$ (fig. 7) indicates that the lowest minima are achieved by clustering the small atoms in the center and accommodating all the large atoms in an external shell. In the particular case illustrated in figure the resulting cluster can be seen as two interpenetrating 9-faced polyhedra each one centred on the small atoms. Such trend seems to be rather general: also figure 8 shows that small atoms tend to for a droplet which becomes the core of the cluster. Both 9-faced and 12-faced polyhedra are of little relevance in the middle of the region, where no structure is found to dominate: the peak of other structures is a mixture of unequal, elongated clusters. It’s worth to note that for all values of $\alpha$ there a visible presence of 12-faces structures at $\eta=1$, even when the low-$\eta$ range is characterized by structures other than 12-faced polyhedra.

Of course the analysis with the Voronoi polyhedra does not tell the whole story. For instance, 12-faced polyhedra can be of different sorts: they can be icosahedra with an L particle at the center, icosahedra with an S-atom at the center, or even irregular, nonicosahedral structures.
C. Icosahedral Structures

There are two different classes of icosahedral clusters: the ones with a small particle in the center of the cage and those built around a large particle. We will call these structures S-ICO and L-ICO respectively. On fig. 2A,B,C,D the S-ICO peaks are marked with an oval, and L-ICO peaks are signed with a rectangle. First we note that for the three lowest $\alpha$’s S-ICO’s are present at low energy for all concentrations, while for $\alpha=1.6$ they can be found only for $\eta > 6$. This observation can be summarized by saying that whenever the energy gap is present, all states below the gap are S-ICO’s (although the presence of a gap for $\alpha=1.4$ is not so obvious at small concentration). L-ICO’s are present only for low $\eta$’s, intermixed with non-icosahedral states: their energy grows rapidly with $\eta$, so that they can never be found for $\eta > 5$ in the energy range we considered: the presence and the importance of this kind of structures is therefore very marginal. Figure 9 summarize this aspect: the lowest L-ICO configurations are plotted as function of the concentration.

It is also interesting to note the number of different S-ICO configurations has a maximum for intermediate concentrations, and it decreases symmetrically when $\eta$ gets larger or smaller.

The number of different icosahedral configurations built around a small particle can be predicted. We can state the problem in the following way: in how many ways can the 13 vertices of an icosahedron be decorated with $\eta$ S-atoms and $13 - \eta$ L-atoms? if no vertices are equivalent the answer is trivial: the number of different decorations will be given by the binomial coefficient. But this is not the case of the regular icosahedral cage: in this case the problem is to calculate the number of different isomers (or different polytypes in mathematical terminology). As an example consider the case of $\eta=1$. In this case we have two different independent arrangements: as first choice we can put the S particle in the center of the cage and the L particles on vertices of the icosahedron. The second possibility is to put an L particle in the center: for the S particle there are therefore 12 topologically equivalent vertices on the external cage: the resulting isomer is therefore 12 times degenerated. The process of deriving all the isomers and the relative degenerations for all $\eta$’s is not a simple
task. The number of different isomers has been recently calculated by Theo and coworkers \cite{1} with an application of the Polya’s enumeration theorem. In table 1 we report, as a function of $\eta$, the number of isomers and the number of different S-ICO’s found for each value of $\alpha$. For the lowest two values of $\alpha$ the number of S-ICO’s coincides with the expected number of isomers: peaks at different energies below the gap are due to different arrangements of L and S-atoms on an icosahedral structure. For $\alpha=1.4$ the ratio between found S-ICO’s and expected isomers drops for values of $\eta$ smaller than 7, as shown in fig. 8. An even more dramatic transition is shown for $\alpha=1.6$, where the ratio drops abruptly from one to zero when $\eta$ decreases from 9 to 6, showing the impossibility to build icosahedra for such radii-ratio when the s-particles are minority.

Interesting observations can arise from the fact that for high values of concentration almost all the isomers are present. We checked to find correlations between the relative positions of L-atoms (considered as impurities in a cluster formed by S-atoms) and the energy or the distortion of the cluster. Our results do not allow a coherent interpretation of all data, but we were able to detect some regularities \cite{16}. Let us first focus on $\eta > 9$, where we find icosahedral isomers for all the values of $\alpha$. For all these structures a general rule is valid: the energy of the isomers is strictly correlated with the disposition of the impurities on the cluster. As a matter of fact in the lowest minima we find structures where the L impurities tend to occupy contiguous positions on the external shell, and the energy grows when the atoms are placed in non adjacent positions. A very clear example is given in the case of two large atoms ($\eta=11$ and 3 different isomers): the lowest configuration is the configuration with impurities placed as first neighbours, the second with L-atoms as second neighbours and the highest one with L-atoms as third neighbours. This situation is the same for all the values of $\alpha$. Decreasing $\eta$ this rule is violated: for $\eta=9$ it remains valid for $\alpha=1.33$ and $\alpha=1.25$ while for $\eta=8$ only the lowest value of $\alpha$ is consistent with this picture. Lowering $\eta$ again no regularities are found. Along this line one can expect that the structures of the icosahedra have a high degree of distortion if the L-atoms are close, while the distortion is small if they are placed in a symmetric way. All the observations of distortion (based on the
measure of the third order invariant) confirm this idea so we can say that the most distorted clusters correspond to the lowest minima. We have to stress that this picture is valid only as long as the L-atoms can be considered as a perturbation on a icosahedron of S-atoms, i.e. for large η’s. A similar rule might be valid also for the case in which S-atoms perturb an icosahedron of L-atoms, but since L-ICO’s are very expensive in energy we do not have samples to verify this idea. With regard to the role of α, it’s easy to guess that the distortion grows with α: our results confirm this conjecture for all the values of concentrations.

D. The case α = 1.6 and η = 1

As we anticipated the case α=1.6 and η=1 is singular: it is therefore interesting to discuss this case in detail, with the help of 3-D images. The lowest energy is much higher than that for η > 1, and the frequency plot shows two twin peaks. However these two peaks are degenerate, in the sense that each is formed by two different structures very close in energy. The four configurations occur with the same frequency. Figures 10A and 10B present the two structures forming lowest energy peak: the clusters have the same basic structure: a cage formed by ten large atoms surrounds a small atom at the center, while the other two large atoms are on a second shell. The two different states are due to a different accommodation of these external atoms. Figures 10C and 10D show the two clusters belonging to the second peak. It’s worth noting that the structures are completely different in that case: the configuration at higher energy is an icosahedron with a large particle in the center while the lower one is formed by the small atom in the center surrounded by only 8 atoms: four atoms are on the second shell of the cluster. We observe none of the four configuration is an S-ICO: the reason of its singularity lies in part on this simple observation. In all cases for α ≤ 1.4 the lowest energy structures are S-ICO’s. The same is true for α=1.6 and η ≥ 6. For α=1.6 and 1 ≤ η ≤ 5 it is possible to construct structures with a droplet of two or three S-atoms at the center (like in fig. 4 and 7), allowing all the L-atoms to be embedded in a first shell around the droplets. However when the size ratio is so large and only one S-atom
is available, putting the small atom at the center forces two large particles on a second shell: these particles have a small coordination and therefore the energy of the cluster is high.

V. DISCUSSION

A. Interpretation of the Results

In a monoatomic system, the best arrangement of 13 atoms is the icosahedron. Our work is aimed to understand if and how this arrangement changes when a 13 atom cluster is composed of two different kinds of atoms. It is useful to remind that an optimal icosahedral configuration is achieved when the radius of the external particles is 1.06 times larger than the radius of the central particle: in an icosahedral cluster made of equal spheres, the spheres on the shell are therefore a bit loose. Let us first focus on the lower $\eta$ values: the $\eta$ small atoms can be seen as a perturbations of a cluster made of L particles. Such perturbation can have opposite effects, depending on whether an S-atom occupies the center of the cluster or not. We consider first the case $\eta=1$ in which the icosahedron has an L particle at the center, while on the vertices there are 11 L-atoms and 1 S-atom. In the monoatomic cluster the particles on the shell are a bit loose: by shrinking the size of an external particle frustration and energy are increased. When $\eta$ grows, so will do frustration and energy. These considerations can explain what we observe: L-ICO clusters are found only for very small $\eta$’s, and their energy grows rapidly with $\eta$. The role of the $\alpha$ parameter is also easy to understand: the larger the difference between the two component in the cluster, the faster the growth in energy. Let us now consider the case $\eta=1$ with the small atom as the central particle of the cluster: in such configuration the external particles are more squeezed than in the monatomic case. A value of $\alpha$ larger than 1 but smaller than 1.06 helps removing the frustration typical of monoatomic systems. For larger values of $\alpha$ frustration is induced by the fact that the small particle at the center is unable to “fill” the space in the cage created by the external particles. Our results show that for a value of $\alpha$ as large as 1.25 the energy
decreases, which means that the overall frustration is diminished, while larger values of $\alpha$ induce a growth in energy. Increasing $\eta$, the new S-atoms must substitute some L-atoms on the external shell, which by shrinking decreases the frustration of the central atom: energy therefore drops. S-ICO’s are therefore favoured in most cases, with a notable exception occurring when $\alpha$ is too large and $\eta$ is small. In such case, less than 12 particles are needed to surround the central atom: the remaining L-atoms end up in a second shell, where their coordination is low and therefore the energy of the cluster grows. This case was discussed in detail in section [IVD]. The transition from icosahedral structures to non icosahedral ones is clearly shown from the shrinking energy gap between the S-ICO’s and other non icosahedral configuration with impurities at the center of the cage. The non icosahedral minima are favoured as the gap in energy becomes smaller and are dominant starting from $\alpha=1.33$.

Let us now consider the high $\eta$ values. Similar but opposite considerations hold. At $\eta=12$ only one L-atom is present: if it was at the center, frustration of the S-atoms on the shell would increase. In fact, we never find L-ICO’s in this range. The other case (the S-atom as central particle) is the dominant one. The presence of L-atoms on the shell increases the density and moves the cluster toward an energetically more convenient configuration. By decreasing $\eta$, this process continues: S-ICO’s are stable in the whole high-$\eta$ region.

At the light of these considerations it is interesting to reconsider figures 3 and 4. As far as the three lowest values of $\alpha$ are concerned, figure 3 shows how the effect of impurities has a strong dependence on the choice of $\alpha$ in the case of small $\eta$’s (i.e. a few impurities of type S), while when the impurities are of type L (large $\eta$’s) the behavior does not strongly depend on $\alpha$. The curve for $\alpha=1.6$ instead shows two different minima, indicating that at small $\eta$’s icosahedra are again the dominant structure, while at large $\eta$’s different kinds of structures play the dominant role. Figure 4 shows how the insertion of small particles changes the monoatomic case: the first substitution of an S-atom on the cluster lowers the gap between icosahedral and non-icosahedral clusters. This gap tends then to grow toward the monoatomic value when more S-atoms are inserted. The parameter $\alpha$ changes the speed in reaching the limit of the monoatomic case. In the case $\alpha=1.6$ this behaviour is found
only at high $\eta$’s because the absence of icosahedra elsewhere.

**B. Comparison with Extended Systems**

We focus now our attention on a set of papers treating the analysis of icosahedral order in extended binary systems. Our aim is to see what degree of agreement exists between the behaviour we described and the presence or absence of icosahedral order detected in the extended system discussed in these works. In table II we report a certain number of papers dealing with the problem of icosahedral order. From the data of the simulations of each of these works we have extrapolated our two parameters $\eta$ and $\alpha$. It is clear that the right comparison with the parameter $\alpha$ is possible only if the interactive potential is a LJ and if the mixed interaction is treated as in our work. Anyway for sake of completeness we reported in the table also studies performed on different systems: in this case the definition of the $\alpha$ has to be done carefully.

Let us first discuss the system which are strictly comparable with our results: LJ systems. We first concentrate on the work of Jónsson and Andersen [17] and of Shumway et al. [5], in which both groups reported a considerable amount of icosahedral order in their samples. The parameters of two simulations are equal and correspond to $\alpha=1.25$ and $\eta=9.6$. Thank to the courtesy of Hannes Jónsson that provide us some configurations we have analyzed carefully some samples from both these works in order to see in more detail what kind of icosahedra are present: we detected in all the samples only S-ICO types of icosahedra. The characteristics of the icosahedra (structures and concentrations) are in perfect agreement with the results discussed previously [18]. Our results are also in excellent agreement with the work by Dasgupta et al. [19]. In their paper they reported absence of long range icosahedral correlation, which at the light of our study is no surprise, since at the values of concentration and radii chosen by them ($\alpha=1.6$, $\eta=6.5$) there can hardly be an icosahedron! Their result should therefore not be taken as a general indication of the absence of icosahedral order in LJ systems.
Finally the comparison between our results and the ones by Ernst et al. [20] gives some interesting notes. Let us discuss what kind of icosahedra should be expected to find in an extended system like the one simulated by the authors at the light of our results. In the region defined by their parameters ($\alpha=1.25$, $\eta=2.6$) we found icosahedral cluster with both S-ICO and L-ICO clusters, with a strong predominance of the former, due to energetic reasons. When we cool down such extended system we would not expect local minima of type L-ICO (due to their high cost in energy). We would instead expect to find a certain number of S-ICO configurations, since these are energetically favoured: however this number could not be very high, because the small concentration of S-atoms which are needed as seeds of such a kind of icosahedra. This picture fits very well with the results of the work performed by Ernst et al. . They in fact say ..the data for $Q_l$ suggest icosahedral simmetry ... and the average in $Q_l$ is less for a pure icosahedron. A similar result is also obtained by Jónnson [21] on an equivalent system (same values of $\alpha$ and $\eta$), in which again only relatively few icosahedral shells are found, and all of them have S-atoms at the center.

Let us now discuss some works with different potential. One of the most interesting paper we found is the one of Qi and Wang [22] in which the authors simulated a $Mg_3Ca_7$ system finding a strong evidence of icosahedral order. they reported a complete cluster analysis identified by the mean of CNA. Having checked that their definition of the polyhedra is equivalent to our Voronoi construction we then can compare our polyhedra with theirs. The main problem in this case is to define the parameter $\alpha$, since the authors did not report the core radius of the pair potential used. We estimate $\alpha$ to be equal to 1.33 where Ca is the L-atom and Mg the small one (this value of the ratio is the same suggested by Nelson [3] for the same system modelled by hard sphere. It is also very close to the ratio of the atomic radii of the two elements.). Also in this case let us imagine what kind of structures would be expected to see in such system based on our findings: with $\alpha=1.33$ and $\eta=4$ we are in zone with dominant S-ICO clusters but with a few other minima of some importance in the gap. So what we expect to see is some icosahedral structures (all with small atoms at the centre) and some other significant minima. This picture agrees with the results by
Qi and Wang partially: the most frequented clusters are coordinate 12, and the structures are icosahedral and \((0,2,8,2,0)\) polyhedra. A rough estimation of the frequency of these polyhedra is qualitatively similar with our frequency of visits. A great majority of the icosahedral cluster has a small atom (Mg) at the center: the surprise however is the existence of some L-ICO structures. The relative absence of low coordination polyhedra is probably due to the difference between an extended system and an isolated cluster: however all the low coordination polyhedra they detected are present in our configurations.

Finally we compare our result with two works performed on hard sphere systems. In this case the natural choice of the parameter \(\alpha\) is given by the ratio of the radii of the two different spheres. Our results fit well with the result of Clarke and Jónnson \cite{23} in which they found icosahedral order in a binary system of hard sphere with parameter \(\alpha=1.25\) and \(\eta=9.6\). In the work of Clark and Wiley \cite{24} in which they explore several concentrations and \(\alpha\) values the results are more difficult to compare directly because the authors do not present extended results for all the points explored and they limit themselves to general considerations concluding that icosahedral order is negligible in all their systems. However extrapolating the data from the figures presented we can detect a qualitative agreement also in this case.

As a final remark we can say that our results show a substantial agreement with all the results presented in literature and can therefore be used as a good indication for predicting the existence of icosahedra (and maybe of icosahedral order) for given size-ratios and concentrations in binary systems.

**VI. CONCLUSION**

We studied 13-atom clusters of binary mixtures at four radii-ratios \(\alpha\) and for all possible concentration \(\eta\) of small particles. We found that icosahedral structures are important for small \(\alpha\) and become less relevant when \(\alpha\) grows: for large values of \(\alpha\) icosahedral structures play a role only when \(\eta\) is large. A general interpretation of this behaviour is given in
term of impurities on the clusters. Finally our results can be successfully compared with the claims of presence or absence of icosahedra in quenched extended binary systems, therefore allowing a better understanding of the contrasting results which appear in literature.

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FIGURES

FIG. 1. The set of the energy spectra for all the points in our space parameter. Figures 1A, 1B, 1C, 1D represent respectively the spectra for $\alpha=1.25, 1.33, 1.4$, and 1.6. Within the same $\alpha$ all the 12 different concentrations are plotted starting with $\eta=1$ (left) and ending with $\eta=12$ (right). The energy scale (the same for all the plots) is the absolute scale of energy and every straight line represent a different minimum. All the minima reported here are detected at least twice in our simulations.

FIG. 2. The histograms of the percentage of visits to the minima. As in figure 1 each of four different figures is for the four different values of $\alpha$ and within the same $\alpha$ all the 12 different values of concentrations are plotted. For a better representation every different value of concentrations is shifted up by a number proportional to $\eta$: the lowest curve is therefore for the lowest concentration ($\eta=1$) while the upper curve is for $\eta=12$. Every peak of the curve is generally formed by more than a single minimum because the relative large bin used in the histograms. All the peaks signed by an oval are due to icosahedral structures with a small atom at the center of the cage and the contribution to those peaks comes completely from icosahedral minima. On the curves we also indicated the positions of the icosahedral minima (squares) with a large atom at the center. In those cases, conversely, the contribution given by the icosahedral structures is not dominant at all.

FIG. 3. The lowest minimum in the spectra plotted as a function of the concentration for the four values of $\alpha$. The energy is in LJ units. The three lower values of $\alpha$ has a similar parabolic shape with the same minumum at $\eta=7$ and all the minima have an icosahedral cage. While the 1.6 case has a double well-shape and the icosahedral structure are limited only for $\eta > 7$.

FIG. 4. The energy gap between the highest minimum in energy of the S-ICO’s structures and the first non icosahedral cluster as a function of the concentrations. The four lines indicate the four different values of $\alpha$. The 1.6 curve is not over all the range because there are icosahedral structure for $\eta < 6$. Energy is given in LJ units.
FIG. 5. In this set of four figures we plot the percentage of the clusters with a Voronoi polyhedra with 12 faces (indicates with 12) as a function of concentration and the percentage of the remaining clusters with less than 12 faces (indicates with others). As usual A B C D refer to $\alpha=1.25$, 1.33, 1.4 and 1.6. For the greater three value of $\alpha$ we plot also the major component of the other curve: for $\alpha=1.33$ and 1.4 the percentage of clusters with the 10-faces Voronoi cage, while for $\alpha=1.6$ the dominant component is given by polyhedra with 9 faces.

FIG. 6. A typical cluster with a Voronoi cage of 10 faces for $\eta=3$ and $\alpha=1.4$. The cage in this case has 2 quadrangular faces and 8 pentagonal faces. The two external particles are indicated in light gray. The central particle here is a small one. Note that the 3 small atoms are all first neighbours.

FIG. 7. The absolute minimum energy cluster for the case $\alpha=1.6$ and $\eta=2$. The two small particles are inside a cage formed by the large particles. The peculhiaty of this structure is that each of the two small particles is at the center of a Voronoi cage of 9 faces. The particles belonging to a such a structure are in the figure in light gray). In dark gray are represented the three particles on the second shell of such a cage.

FIG. 8. The ratio between the number of different icosahedral minima detected for $\alpha=1.4$ and 1.6 and the number of isomers as a function of concentrations. All the icosahedral minima are of S-ICO-type.

FIG. 9. The energy of the lowest L-ICO structures as a function of the concentration $\eta$. The four symbols are for the different values of $\alpha$. The rapid increasing in energy as $\eta$ grows limits the range of presence of such structures at very low concentrations.
FIG. 10. The four different structure of the lowest minima for the case $\alpha=1.6$ and $\eta=1$. Fig A and B are the lowest two, with the same Voronoi cage (0,2,8,0,0): in this case the small differences in energy is given by the different positions on the second shell of the two remaining particles. Figure C is the perfect icosahedron with the small particle on the external shell and with a large particle at the center while figure D shows the last minimum in which the small particle is surrounded by only few atoms L, and the remaining atoms take place on the second shell.
TABLES

TABLE I. The table presents the number of different isomers for an icosahedron having a particle S at the center, and $13 - \eta$ atoms of the second kind (L) distributed on external vertices. The number of isomers is then compared with the number of different icosahedral minima (with S particle at the center) detected for all the values of $\alpha$.

| $\eta$ | isomers | $\alpha=1.6$ | $\alpha=1.4$ | $\alpha=1.33$ | $\alpha=1.25$ |
|-------|--------|-------------|-------------|-------------|-------------|
| 1     | 1      | 0           | 1           | 1           | 1           |
| 2     | 1      | 0           | 1           | 1           | 1           |
| 3     | 3      | 0           | 1           | 3           | 3           |
| 4     | 5      | 0           | 3           | 5           | 5           |
| 5     | 10     | 0           | 7           | 10          | 10          |
| 6     | 12     | 0           | 9           | 12          | 12          |
| 7     | 18     | 2           | 17          | 18          | 18          |
| 8     | 12     | 5           | 12          | 12          | 12          |
| 9     | 10     | 9           | 10          | 10          | 10          |
| 10    | 5      | 5           | 5           | 5           | 5           |
| 11    | 3      | 3           | 3           | 3           | 3           |
| 12    | 1      | 1           | 1           | 1           | 1           |
TABLE II. A collection of papers dealing with the problem of icosahedral order in binary systems. Column one gives the authors, column two specifies the interatomic potential used in simulations. The percentage of S particles used by the authors is given in column 3, and in column 4 as $\eta$, to facilitate the comparison with the present work. Column 5 indicates the value of the size ratio ($\alpha$), and column 6 gives an indication about icosahedra detected in the samples.

| Authors                      | potential | % of S-atoms | $\eta$ | $\alpha$ | icosahedra? |
|------------------------------|-----------|--------------|--------|----------|-------------|
| Jónsson and Andersen (ref. [17]) | LJ        | 80%          | 9.6    | 1.25     | YES         |
| Shumway et al. (ref [5])     | LJ        | 80%          | 9.6    | 1.25     | YES         |
| Dasgupta et al. (ref [19])   | LJ        | 50%          | 6.5    | 1.6      | NO          |
| Ernst et al. (ref. [20])     | LJ        | 20%          | 2.6    | 1.25     | Suggested   |
| Qi and Wang (ref [22])       | Mg3Ca7    | 70%          | 3.9    | 1.33     | YES         |
| Clarke and Wiley (ref [24])  | hard-spheres | various   | various | 1.1 - 1.5 | Negligible |
| Clarke and Jónsson (ref [23]) | hard-spheres | 80%       | 9.6    | 1.25     | YES         |