

Method for Simultaneous Prediction of Atomic Structure and Stability of Nanoclusters in a Wide Area of Compositions

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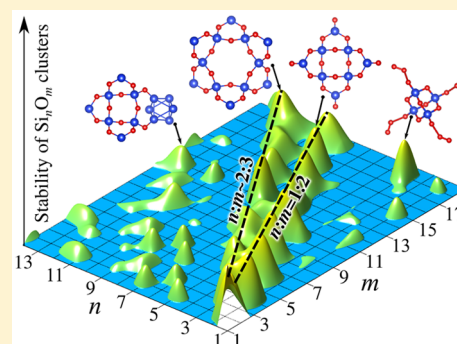
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Supporting Information

ABSTRACT: We present a universal method for the large-scale prediction of the atomic structure of clusters. Our algorithm performs the joint evolutionary search for all clusters in a given area of the compositional space and takes advantage of structural similarities frequently observed in clusters of close compositions. The resulting speedup is up to 50 times compared to current methods. This enables first-principles studies of multicomponent clusters with full coverage of a wide range of compositions. As an example, we report an unprecedented first-principles global optimization of 315 Si_nO_m clusters with $n \leq 15$ and $m \leq 20$. The obtained map of Si–O cluster stability shows the existence of both expected $(\text{SiO}_2)_n$ and unexpected (e.g., Si_4O_{18}) stable (magic) clusters, which can be important for a variety of applications.



The unique properties of nanoparticles are extensively used in optoelectronics, photovoltaics, photocatalysis, biomedicine, etc. These properties are closely linked to the atomic structure of particles, especially in small particles and nanoclusters.^{1,2} Despite the importance of knowing the structure, its experimental determination remains very difficult.³ For this reason the main body of structural information on clusters is obtained via first-principles calculations⁴ that were mostly done either for monatomic clusters or for binary clusters of stoichiometric composition corresponding to the bulk compounds, whereas clusters of general composition were studied in only a few publications.^{5,6} Such a focus in *ab initio* research ignores the fact that the chemistry of clusters is much richer than that of solids because of a large share of surface atoms. Multicomponent clusters often have stable compositions that are far from chemical compounds presented in the bulk x – T phase diagram. This is of interest not only for basic chemistry of clusters. It significantly increases the scope of candidate nanomaterials for practical applications, such as the development of efficient and affordable catalysts^{7,8} and magnets,⁹ the investigation of complex processes of nucleation and particle growth,^{10–12} etc.

The bottleneck of first-principles study of nanoclusters is the computational cost of cluster structure prediction, which is a global optimization of the total energy among all possible atomic configurations. There are several methods of structure prediction (basin and minima hopping,^{13,14} simulated annealing,¹⁵ evolutionary algorithm,¹⁶ etc.); however, they all involve thousands of local optimizations (relaxations) even for finding a structure of one cluster. Given the existence and

importance of unexpected cluster compositions, cluster structure prediction and the screening of stability and properties are required in wide regions including hundreds of cluster compositions; therefore, such first-principles investigations turn out to be extremely demanding. To reduce the computational cost, the global optimization is often performed in combination with semiempirical methods or force fields.^{17,18} Success depends greatly on the model potential, which is often difficult to make sufficiently accurate. Here we suggest a different approach to this problem, which does not invoke semiempirical potentials at all. Our method simultaneously predicts all clusters in the whole given area of compositions in a highly efficient manner that incorporates exchange of structural information, i.e., learning between clusters of different compositions. The effectiveness of our approach is based on the frequent similarity of structural motifs in clusters of close compositions. We will refer to our technique as variable-composition cluster search in contrast to the previous, fixed-composition approaches.

Our method is derived from the evolutionary algorithm implemented in the USPEX code,^{16,19,20} which proved to be successful for predicting novel materials.^{21,22} Briefly, the algorithm is based on the analogy with natural evolution: first population of structures (the first generation) is created randomly and locally optimized. A certain percentage of the best structures serve as parents for the next generation, which

Received: November 20, 2018

Accepted: December 18, 2018

Published: December 18, 2018

is produced using the so-called variation operators: crossover, mutations, etc. Then the newly produced generation is locally optimized and so on, until global minimum is found.

Our technique performs a joint evolutionary search for the whole given area of compositions at the same time. It required two major innovations. First, the selection of the fittest configurations (selecting best parents) is performed on equal footing for clusters of all compositions. Second, we developed new variation operators to provide the transfer of structural information between clusters of different compositions.

Let us consider the new selection procedure in more detail. It is grounded in the notion of “magic” clusters. We classify a cluster as magic if a pair of such clusters is stable against the transfer of one atom between them. Giving it a formal description, we denote the composition of a cluster with the formula $X_{n_1}Y_{n_2}\dots Z_{n_k}$ by a vector $\mathbf{n} = (n_1, n_2, \dots, n_k)$. If an atom of sort s is added or removed, the composition becomes $\mathbf{n}_s^\pm = (n_1, \dots, n_s \pm 1, \dots, n_k)$. The cluster is magic if the second-order differences of the energy

$$\Delta_{ss}E(\mathbf{n}) = E(\mathbf{n}_s^+) + E(\mathbf{n}_s^-) - 2E(\mathbf{n}) \quad (1)$$

are positive for all atomic types s . Having the (nonregular) set of magic compositions, we build the reference energy surface $E_{\text{ref}}(\mathbf{n})$ as a piecewise linear interpolation of “magic” energies over all given areas of compositions. A configuration is classified as “best” and selected to participate as a parent for the next generation if its energy falls in the interval $E_{\text{conf}}(\mathbf{n}) - E_{\text{ref}}(\mathbf{n}) \leq \Delta E_{\text{sel}}$. The interval ΔE_{sel} is defined so that the share of the best configurations is $N^{\text{best}}/N \approx 0.6-0.8$. We note that the global thermodynamic stability of clusters is not required, as any cluster system is unstable with respect to growth or coalescence; the only truly thermodynamically stable cluster is the infinite one, i.e., a crystal. This situation is totally different from the variable-stoichiometry prediction of crystalline structures,²³ which provides only the thermodynamically stable phases.

Our method uses all variation operators of the standard fixed-composition approach:²⁰ (1) creating structures with randomly picked point symmetries, (2) permutations of chemically different atoms, (3) softmutation (displacement of atoms along eigenvectors of the softest vibrational modes), and (4) heredity (creating child structure from fragments of two parents). Among these operators, only heredity is suitable for structural exchange between clusters of different compositions and was modified accordingly. To further enhance such exchange, three new variation operators are introduced: (5) transmutation (change of chemical identity of randomly selected atoms), (6) removal of one atom from the cluster, and (7) addition of one atom to the cluster.

For operators 6 and 7, the site where one atom should be removed or added is of importance. The choice of an atom i to be removed is defined by its effective coordination number O_i :

$$O_i = \frac{\sum_j \exp(-(r_{ij} - R_i - R_j)/d)}{\max_j \exp(-(r_{ij} - R_i - R_j)/d)} \quad (2)$$

where r_{ij} is the distance between atoms i and j ; R_i and R_j are the covalent radii of atoms i and j depending only on their chemical identities;²⁴ $d = 0.23 \text{ \AA}$ is the empirically determined parameter. The i th atom is removed with a probability p_i proportional to $\max_{i \in s} [O_i] - O_i$, where s is the identity of an atom i . Thus, the removal of weakly bound atoms is preferable.

The same applies to the choice of an atom to which an additional atom should be attached. Such atom addition enhances coupling between a weakly bound atom and the remainder of the cluster that gives the maximum gain in binding energy. In addition, our algorithm allows the addition or removal of two atoms simultaneously. This can be useful for systems that prefer an even number of atoms of a particular sort.

We note that the new atomic addition/removal operators usually do not create new structural motifs but spread the good ones between different compositions, thus providing the thorough exploration of the low-energy areas of the landscape. Other operators, considering their greater stochasticity, are responsible for a sufficient level of structural diversity. Such an approach provides a balance between scattering of trials for the effective sampling of search space and focusing on the most promising regions, which is crucial for any heuristic optimization scheme.

The seven variation operators show varying efficiency for different systems and even at different stages of evolutionary search. To take this into account, we implemented the parameter control procedure which changes on-the-fly the number of offspring produced by each operator considering their efficiency at previous stages of the search.²⁵ To increase structural diversity, our method uses yet another, very powerful tool, namely, antiseeds.²⁰ It gives energy penalty for structures that are best for too many generations. This allows one to reliably determine structures of all nonmagic clusters belonging to the area of compositions, as well as low-energy isomer structures.

One may recall that many researchers tried to exploit structural similarity of clusters of close compositions by hand.^{10,26-28} However, the number of possible configurations is still extremely large. For this reason such manual sampling requires too much effort and often fails. In contrast, our method makes similar sampling fully automatic, integrating it into the general evolutionary process. Combined functioning of all variation operators, the new selection scheme, the antiseed technique, and other features give a synergistic effect that results in the high performance of our method.

We test our technique on two model systems: Lennard-Jones clusters with 30–60 atoms and Si_nO_m clusters ($n = 6-8$ and $m = 10-16$) within the semiempirical MNDO approach as implemented in the MOPAC package.²⁹ We compare the convergence speed of the new approach with the standard fixed-composition technique implemented in the USPEX code.²⁰ Figure 1 shows the energy deviations from the ground state averaged over all compositions as a function of the number of relaxations for both methods. This integral characteristic of the convergence rate shows a great speedup of the new method (~ 5 times for LJ clusters and up to 50 times for Si_nO_m clusters). A more thorough analysis presented in the Supporting Information shows high efficiency of new variation operators which produce most of the low-energy offspring of the new method.

As the first real application, we chose Si_nO_m clusters owing to their practical importance and great structural diversity (crystalline silica alone has 14 structural forms). The search was performed at the *ab initio* level within the unprecedentedly wide range of compositions ($1 \leq n \leq 15$ and $0 \leq m \leq 20$, i.e., 315 cluster compositions). We note that the earlier investigations of Si_nO_m were either done for relatively small clusters ($n \leq 7$)^{6,26,28,30,31} or focused on stoichiometric

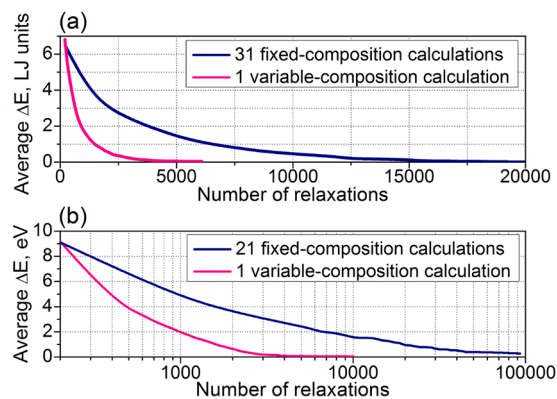


Figure 1. Convergence rate of variable- and fixed-composition methods. Energy deviations from the ground states averaged over all compositions as a function of number of relaxations is given for (a) Lennard-Jones clusters with 30–60 atoms and (b) Si_nO_m clusters ($n = 6\text{--}8$ and $m = 10\text{--}16$) calculated by the MNDO method (the logarithmic scale is used).

compounds $(\text{SiO})_n$ or $(\text{SiO}_2)_n$.^{4,10,27,32,33} Even for these compositions it is often seen that newer papers report lower-energy structures than the older ones. As an example, we mention recent study of $(\text{SiO})_n$ clusters which were constructed “by hand”, joining fragments of $(\text{SiO}_2)_n$ and Si_n clusters together.¹⁰ Surprisingly, these structures turned out to be better than those reported in all previous studies using global optimization techniques.

We perform our global optimization combined with density functional calculations within the PAW–PBE approximation implemented in the VASP code.^{34,35} The energies of the 10 best structures for each composition were refined using the Gaussian code³⁶ with the B3LYP/6-311+G(2d,p) approach.³⁷ Comparison of our results with earlier publications^{4,6,10,26–28,30–33} showed that for 101 Si_nO_m compositions we found the same global minima as previously published, for 17 compositions we found lower-energy structures, and 197

cluster compositions were studied for the first time to our best knowledge (see Table S1). Figure 2 shows Si_nO_m stable (magic) clusters which are divided into four groups discussed below. The optimal structures of all 315 clusters are given in Table S2.

Scanning over wide composition areas reveals trends in cluster structure and related properties. To illustrate this point, we explore the stability patterns of Si_nO_m clusters using two criteria. The first one characterizes the resistance toward the transfer of Si or O atoms between clusters. It calculates second-order differences over Si and O atoms ($\Delta E_{mn}(n, m)$ and $\Delta E_{mm}(n, m)$ of eq 1) and takes the minimal one: $\Delta_{\min}(n, m) = \min\{\Delta_{mn}E(n, m), \Delta_{mm}E(n, m)\}$. The second criterion calculates dissociation energies for all possible fragmentation channels $\text{Si}_n\text{O}_m \rightarrow \text{Si}_k\text{O}_l + \text{Si}_{n-k}\text{O}_{m-l}$ with $0 \leq k \leq n$ and $0 \leq l \leq m$:

$$E_{\text{diss}}(n, m, k, l) = E(k, l) + E(n - k, m - l) - E(n, m) \quad (3)$$

and picks the lowest of them: $E_{\text{diss}}(n, m) = \min_{k,l}\{E_{\text{diss}}(n, m, k, l)\}$. The higher $E_{\text{diss}}(n, m)$, the more resistant to fragmentation the cluster. In stable clusters, both $\Delta_{\min}(n, m)$ and $E_{\text{diss}}(n, m)$ should be positive, while a negative value of $\Delta_{\min}(n, m)$ or $E_{\text{diss}}(n, m)$ is a sign of instability.

Figure 3 shows the contour maps of calculated $\Delta_{\min}(n, m)$ and $E_{\text{diss}}(n, m)$ as functions of n and m . In both figures, the areas of high stability look like mountain ridges or islands. As expected, silica $(\text{SiO}_2)_n$ clusters are highly stable according to both criteria. Surprisingly, Si_nO_m clusters with $n \approx 2/3m$ exhibit comparable stability. These clusters (Figure 2a) resemble $(\text{SiO}_2)_n$ (Figure 2c) but are constructed of Si–O–Si bridges only and have no Si=O double bonds. As seen in Figure 3a, there are also several minor stability islands running along $n \approx 4 + 2m/3$, $n \approx 6 + 2m/3$, and $n \approx 10 + 2m/3$. Such nonstoichiometric compounds are also rather stable according to the second criterion (Figure 3b). They contain excess of silicon, which segregates as a compact group of Si atoms, attached to the skeleton of Si–O bonds only (see Figure 2b). Such clusters are of interest because of experiments on growth

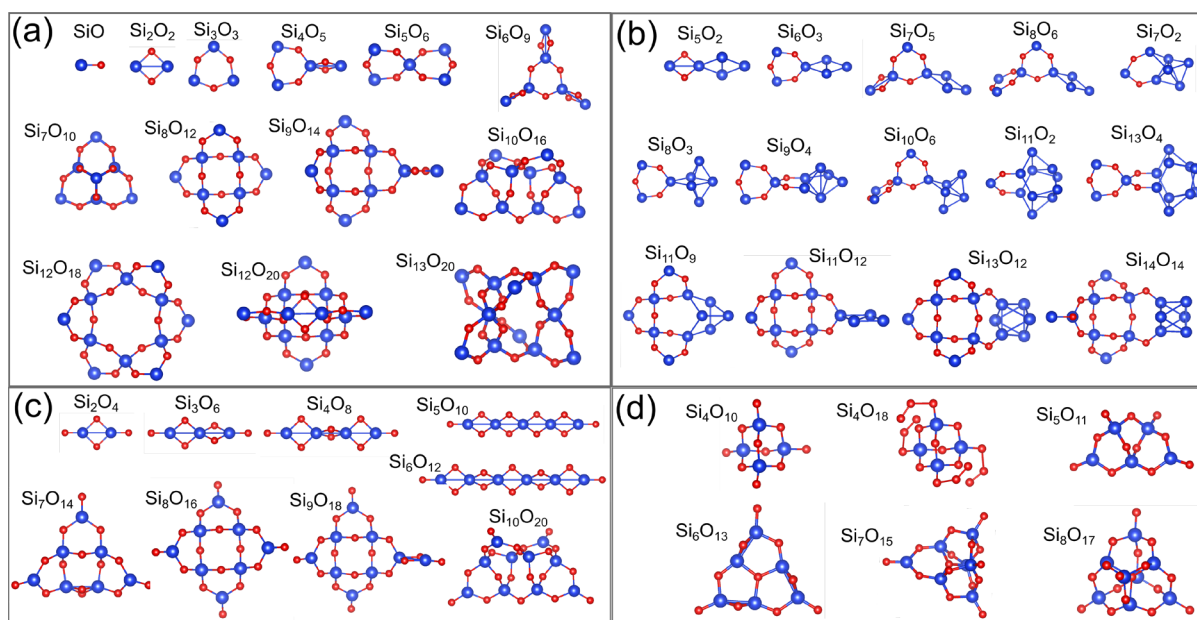


Figure 2. Optimal structure of selected stable Si_nO_m clusters, divided into four groups: the most stable clusters with (a) $n:m \approx 2:3$ and (c) $n:m = 1:2$; (b) silicon-rich clusters and (d) superoxidized clusters ($m \geq 2n + 1$).

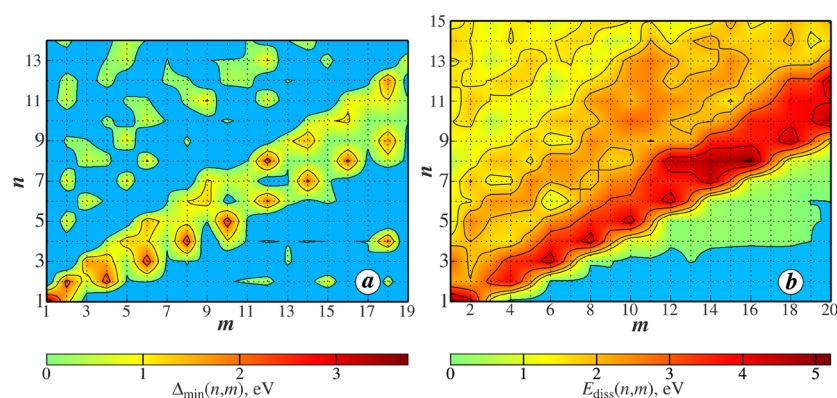


Figure 3. Relief map of stability in Si_nO_m clusters according to two criteria: (a) $\Delta_{\min}(n, m)$ (in eV) as a function of n and m , showing resistance to transfer of Si or O atom between two identical clusters; (b) $E_{\text{diss}}(n, m)$ showing resistance to dissociation into fragments. Regions of instability are marked in blue.

of long silicon nanowires from gas-phase SiO .¹¹ Another interesting class of stable compounds is superoxidized Si_4O_{10} and $\text{Si}_n\text{O}_{2n+1}$ ($n \geq 5$) clusters (see Figure 2d). The latter have relatively low values of Δ_{\min} but quite high values (2.5–3 eV) of $E_{\text{diss}}(n, m)$. We also distinguish the Si_4O_{18} cluster, which is notably stable by the first criterion. Interestingly, this cluster is similar to the recently synthesized P_4O_{18} cluster³⁸ but has free-ending O_3 groups instead of closed ones in P_4O_{18} (see Figure 2d). The important feature of superoxidized clusters is spin-polarized groups with O–O bonds providing their high reactivity, which may determine the toxicity of silica particles.^{6,39}

The exploration of $(\text{SiO})_n$ clusters is of interest for astrophysics because of the presence of SiO molecules in the circumstellar space and their role in the formation of silicates. We note that these clusters do not form a distinct range of Δ_{\min} or E_{diss} . For this reason they can transform to neighboring, more stable clusters that should be taken into account when interpreting their optical signatures.

In conclusion, we have developed a new method for simultaneous prediction of structures of clusters in vast areas of compositions. In comparison to currently used methods, our approach demonstrated 5–50 times speedup, allowing for massive *ab initio* calculations of nanoclusters at a reasonable cost. The availability of such an efficient tool opens the door to wide exploration of trends in chemistry of multicomponent nanoclusters; to study cluster features connected with the bulk x – T phase diagram; and to the search for new, non-stoichiometric “islands of stability”, which can be interesting for applications. These prospects for nanomaterials science are supported by our first-principles study of Si_nO_m clusters in a very wide range of compositions. We present the overall picture of stability in these clusters and show numerous ridges and islands of stability, which are very distinct from well-studied silica clusters. We hope this first attempt gives strong impetus to wide *ab initio* research into the plethora of important multicomponent cluster systems with rich chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b03510.

Convergence tests performed on Lennard-Jones clusters; ground-state structures of Si_nO_m clusters calculated at *ab initio* level (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.R.O. is supported by the Russian Science Foundation (No. 16-13-10459). We also thank Russian Foundation for Basic Research (Nos. 19-02-00394, 18-32-00991, 16-02-00612 and 17-02-00725). Calculations were performed on the Rurik supercomputer at MIPT, MVS-10p cluster at the Joint Supercomputer Center (Russian Academy of Sciences, Moscow, Russia), and Lobachevsky cluster at the University of Nizhny Novgorod.

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