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Additional Information

Zeolite structure determination using genetic algorithms and geometry optimisation.

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Abstract

A recently presented software, zeoGAsolver, based on genetic algorithms has been updated with new crossover and selection operators that maintain the size of the population in successive iterations while improving the average fitness. Using the density, cell parameters, and symmetry (or candidate symmetries) of a zeolite sample whose resolution can not be achieved by analysis of the XRD (X-Ray Diffraction) data, the software attempts to locate the coordinates of the T-atoms of the zeolite unit cell employing a function of 'fitness' (F), which is defined through the different contributions to the 'penalties' (P) as $F = 1/(1+P)$. While testing the software to find known zeolites such as LTA (Zeolite A), AEI (SSZ-39), ITW (ITQ-12) and others, the algorithm has found not only most of the target zeolites but also seven new hypothetical zeolites whose feasibility is confirmed by energetic and structural criteria.

1. Introduction.

The design of new solid state materials is strongly based on our knowledge of the general rules which dictate order at the short and long range in matter. In zeolites, with both covalent (short range) and ionic (long range) factors playing an important role, the rigidity of the tetrahedral primary building units is in stark contrast with the flexibility of the relative orientations of such tetrahedra. This flexibility is the reason of the large number of existing zeolites, and can be numerically studied through the analysis of T-T-T (T = Si,Al) angles¹.

Additionally to the database of zeolites compiled by the IZA², also hypothetical zeolites (either feasible or not feasible) have been proposed. In spite of exhaustive investigations since the first databases of hypothetical zeolite structures were presented^{3 4 5 6 7 8}, we still wonder about the rules that nature dictates to allow ones and restrict others from the reduced set of **feasible zeolites**, those that have been or might be synthesised. Criteria of zeolite feasibility, presented below, can be combined with hypothetical zeolites in order to generate new zeolites using computer algorithms, which is the main aim of the present study.

Roman-Roman and Zicovich-Wilson⁹, similarly to earlier ideas by O'Keeffe and Hyde¹⁰, pointed the crucial role played by the long-range forces that operate in zeolites and contribute significantly to its stability, and also explain the relative instability of large voids. Large micropores are however possible, provided that they are sustained by thick pillars. In the chemical language, large micropores need the vicinity of high density regions.

This concept is based on the old and most successful idea by Brunner and Meier¹¹ that very small rings are needed when very large rings are present. Almost 30 years later, no zeolites have been found to contradict the postulated lower threshold of density versus 'average size of smallest ring'. Less dense structures than those predicted by Brunner and Meier might

¹ X. Liu, S. Valero, E. Argente, V. Botti and G. Sastre; The importance of T...T...T angles in the feasibility of zeolites; *Z. Kristallogr.* **2015**; 230, 291–299.

² Ch. Baerlocher, L. B. McCusker and D. H. Olson; *Atlas of Zeolite Framework Types*, 6th Revised Edition, Elsevier **2007**. (176 structures). The web version [www.iza-structure.org] contains currently 232 structures.

³ M. M. J. Treacy, K. H. Randall, S. Rao, J. A. Perry and D. J. Chadi; Enumeration of Periodic Tetrahedral Frameworks; *Z. Kristallogr.* **1997**; 212, 768–791.

⁴ O. Delgado-Friedrichs and D. H. Huson; Tiling space by platonic solids; *Discrete Comput. Geom.* **1999**, 21, 299–315.

⁵ O. Delgado-Friedrichs, A. W. M. Dress, D. H. Huson, J. Klinowski and A. L. Mackay; Systematic enumeration of crystalline networks; *Nature* **1999**, 400, 644–647.

⁶ M. M. J. Treacy, I. Rivin, E. Balkovsky, K. H. Randall and M. D. Foster; Enumeration of periodic tetrahedral frameworks. Polynodal graphs; *Micropor. Mesopor. Mater.* **2004**, 74, 121–132.

⁷ M. D. Foster and M. M. J. Treacy; Database of Hypothetical Zeolite Structures: http://www.hypotheticalzeolites.net/NEWDATABASE/SILVER_UNIQ/query.php

⁸ D. J. Earl and M. W. Deem; Toward a Database of Hypothetical Zeolite Structures; *Ind. Eng. Chem. Res.* **2006**, 45, 5449–5454.

⁹ E. I. Román-Román and C. M. Zicovich-Wilson; The role of long-range van der Waals forces in the relative stability of SiO₂ zeolites; *Chem. Phys. Lett.* **2015**, 619, 109–114.

¹⁰ M. O'Keeffe and B. G. Hyde; The role of nonbonded forces in crystals; *Structure and Bonding in Crystals*, Vol. 1, Chapter 10, pp. 227–254. Academic Press **1981**, New York.

¹¹ G. O. Brunner and W. M. Meier; Framework density distribution of zeolite-type tetrahedral nets; *Nature* **1989**, 337, 146–147.

however be feasible if a large number of small rings is present. This is the argument employed by Zwijnenburg and Bell¹², where several hypothetical zeolites containing a large percentage of 4-rings are proposed, giving low density and stable energetics, even below 11.8 T-atoms/Å³, the smallest density predicted by Brunner and Meier for zeolites whose average size of smallest ring is 4-ring.

A different criterium has been defined in terms of structural factors extracted from zeolites optimised with a force field¹³. For silica zeolites, eight mathematical equations involving O...O, T...T, and T-O distances are proposed in the so called LID-criteria (local interatomic distances). Unlike the energetic criterium which is highly dependent on the methodology, this is a more general definition although numerically the boundaries can always be subject to controversy. In general, these and other definitions work well for the most stable structures, and so in that region they can safely determine feasibility. However, in the less stable region there is not any algorithm that can ensure that a structure is not feasible. The existence of RWY zeolite, widely assessed amongst the most energetic (and less feasible!) is a proof that algorithms work confidently only in one direction: meeting the criteria means 'feasible', but not meeting the criteria does not necessarily mean 'unfeasible'.

Our zeoGAsolver software, based on genetic algorithms, has been presented recently^{14 15} and will not be explained in detail. The initial aim is to help with synthesised structures which can not be determined with the algorithms for the treatment of the XRD (X-Ray Diffraction) spectrum. ZeoGAsolver tries to find the atomic coordinates of the unit cell using as input the cell parameters, some candidate space groups, and the material density. Coupled with an automated generation of cell parameters and by dealing with the material density as a variable the software has been used to generate hypothetical zeolites belonging to several implemented space groups and it is under development to implement all 230 space groups. Further, only zeolite structures with up to four inequivalent T-sites have been successfully obtained by the current version of the software. Hence it has been possible to obtain success in a number of tests aimed to determine known zeolites such as LTA, NPT, BIK, AFO, AHT, AEI, ATS, CDO, RTH, STF, and ITW. And, while running these tests, other new zeolites have been obtained by a combination of the ZeoGAsolver plus a new functionality based on geometry optimisation that we describe in this study.

¹² M. A. Zwijnenburg and R. G. Bell; Absence of Limitations on the Framework Density and Pore Size of High-Silica Zeolites; *Chem. Mater.* **2008**, 20, 3008–3014.

¹³ Y. Li, J. Yu and R. Xu; Criteria for Zeolite Frameworks Realizable for Target Synthesis; *Angew. Chem. Int. Ed.* **2013**, 52, 1673–1677.

¹⁴ X. Liu, S. Valero, E. Argente and G. Sastre; Determining zeolite structures with a domain-dependent genetic algorithm; *Iberian Conference on Information Systems and Technologies, CISTI 2017*; DOI: 10.23919/CISTI.2017.7976059

¹⁵ X. Liu, E. Argente, S. Valero and G. Sastre; Applying Genetic Algorithms in Chemical Engineering for Determining Zeolite Structures; *Advances in Intelligent Systems and Computing* **2018**, 649, 34-43. DOI: 10.1007/978-3-319-67180-2_4

2. Methods.

2.1. zeoGAsolver. The software works using the symmetry of the crystal and it needs only to find the location of as many T-atoms as those present in the asymmetric unit. The program employs a 'fitness' (F) function specifically defined including the different contributions to the 'penalties' (P) as $F = 1/(1+P)$, with:

$$P = w_{SG} \times P_{SG} + w_D \times P_D + w_{TC} \times P_{TC} + w_{GC} \times P_{GC} + w_A \times P_A + w_{AA} \times P_{AA} + w_{TP} \times P_{TP} + w_M \times P_M$$

Where each penalty is multiplied by its corresponding weight (w), used to normalise the results of each penalty. The penalties include: space group (SG), density (D), tetra coordination either local (TC) or global (GC), angles either individual (A) or averaged (AA), tetrahedron planarity (TP) and molecularity (M).

The initial atomic coordinates in the asymmetric unit are not totally random since they are forced to comply with requirements of the space group such as the number of special positions and the limiting values of the atomic coordinates. Then, an iterative process starts using a genetic algorithm containing hybrid operators (that combine the effects of crossover and mutation) and selection operators that maintain the size of the population in successive iterations while improving the average fitness. A successful execution is characterised by the generation of a set of T-atoms (CIF file) with F very close to unity.

2.2. Geometry optimisation. A modified version of zeoTsites^{16 17 18} software has been adapted by including the feature of adding oxygen atoms to the T-only cells, taking into account the cell boundaries. A linux script is applied to the resulting that performs a geometry optimisation of the unit cells using four different force fields and also performs a topological analysis to test if the resulting zeolites belong to the IZA database. The script calculates the zeolite feasibility with the LID¹³ criteria and also the energies with respect to quartz.

2.3. Force fields employed. Four force fields have been selected, taking into account different styles and parameterisation strategies. The force field by Bushuev and Sastre¹⁹ (**BS**), developed for silicates and extended to alumino-silicates and silico-alumino-phosphates^{20 21}, employs Lennard-Jones functions for the Si---O and O---O interactions, avoiding the wrong behaviour at close distances of the Buckingham function. The force field employs partial

¹⁶ G. Sastre and J. D. Gale; ZeoTsites: a code for topological and crystallographic tetrahedral sites analysis in zeolites and zeotypes. *Micropor. Mesopor. Mater.* **2001**, 43, 27-40.

¹⁷ G. Sastre and A. Corma; Topological Descriptor for Oxygens in Zeolites. Analysis of Ring Counting in Tetracoordinated Nets; *J. Phys. Chem. B* **2009**, 113, 6398-6405.

¹⁸ D. Bermudez and G. Sastre; Calculation of pore diameters in zeolites; *Theor. Chem. Acc.* **2017**, 136, 116.

¹⁹ Y. G. Bushuev and G. Sastre; Feasibility of Pure Silica Zeolites; *J. Phys. Chem. C* **2010**, 114, 19157–19168.

²⁰ G. Sastre; Computational study of diffusion of propane in small pore acidic zeotypes AFX and AEI; *Catal. Today* **2014**, 226, 25–36.

²¹ A. Ghysels; S. L.C. Moors, K. Hemelsoet, K. De Wispelaere, M. Waroquier, G. Sastre and V. Van Speybroeck; Shape-Selective Diffusion of Olefins in 8-Ring Solid Acid Microporous Zeolites; *J. Phys. Chem. C* **2015**, 119, 23721–23734.

charges ($Q_{\text{Si}} = 2.1$) and three body harmonic terms for O-Si-O (with eq. at 109.47°) and Si-O-Si (with eq. at 142°) bond angles. This force field is particularly accurate to calculate the relative energies of zeolites. Two core-shell (for oxygens) force fields with formal charges ($Q_{\text{Si}} = 4.0$) were used, developed by Sanders, Leslie, Catlow²² (**SLC**), and a derivative by Sastre and Corma²³ (**SC**). They both employ Buckingham functions for the Si---O and O---O interactions as well as a harmonic function for the O-Si-O angles. **SLC** does not include a bonding term for the Si-O-Si angles whilst **SC** includes a screened Vessal anharmonic function. Most parameters remain similar in **SC** with respect to **SLC**, and although the O---O Buckingham parameters are markedly different, above 2 Å the interaction is controlled by electrostatics, with both terms behaving similarly. The differential behaviour between these two core-shell force fields is in the Si-O-Si term, present in **SC** and absent in **SLC**. The fourth force field employed, by Vessal, Leslie, Catlow²⁴ (**VLC**), was parameterised for amorphous silica, with formal charges (like **SLC** and **SC**), an anharmonic term for the O-Si-O angles, and using a rigid ion model (like **BS**).

These force fields were parameterised using mainly structural properties, widely available for tectosilicates and zeolites^{25 26}, and have been largely tested giving good accuracy^{27 28}.

3. Results and discussion.

3.1. Candidate zeolites found by zeoGAsolver. From the candidate zeolites found by the software, those containing 3-rings were not considered, following the strategy by Baumes and coworkers^{29 30}, since they are rarely found as all-silica or alumino-silicate compositions, which are of interest for applications in catalysis and separation³¹. zeoGAsolver has found 28 new zeolites whose smallest ring is 4-ring, corresponding to the space groups numbers 12, 63, and 221, and with 1-4 unequivalent T-sites in the asymmetric unit.

²² M. J. Sanders, M. Leslie, and C. R. A. Catlow; Interatomic potentials for SiO₂; J. Chem. Soc. Chem. Comm. **1984**; 1271-1273.

²³ G. Sastre and A. Corma; Rings and strain in pure silica zeolites. J. Phys. Chem. B **2006**, 110, 17949-17959.

²⁴ B. Vessal, M. Leslie, and C. R. A. Catlow; Molecular Dynamics Simulation of Silica Glass; Mol. Simul. **1989**, 3, 123-136.

²⁵ M. O'Keefe and B. G. Hyde; On Si-O-Si configurations in silicates; Acta Cryst. B **1978**, 34, 27-32.

²⁶ D. S. Wragg, R. E. Morris and A. W. Burton; Pure Silica Zeolite-type Frameworks: A Structural Analysis; Chem. Mater. **2008**, 20, 1561-1570.

²⁷ J.-R. Hill, C. M. Freeman and L. Subramanian; Use of force fields in materials modeling; Rev. Comput. Chem. **2000**, 16, 141-216; Eds. K. B. Lipkowitz and D. B. Boyd; Wiley-VCH, New York.

²⁸ A. F. Combariza, D. A. Gomez and G. Sastre; Simulating the properties of small pore silica zeolites using interatomic potentials; Chem. Soc. Rev. **2013**, 42, 114-127.

²⁹ L. A. Baumes, F. Kruger, S. Jimenez, P. Collet and A. Corma; Boosting theoretical zeolitic framework generation for the determination of new materials structures using gpu programming; Phys. Chem. Chem. Phys. **2011**, 13, 4674-4678.

³⁰ O. Abdelkafi, L. Idoumghar, J. Lepagnot, J.-L. Paillaud, I. Deroche, L. Baumes and P. Collet; Using a novel parallel genetic hybrid algorithm to generate and determine new zeolite frameworks; Comput. Chem. Eng. **2017**, 98, 50-60.

³¹ B. C. Knott, C. T. Nimlos, D. J. Robichaud, M. R. Nimlos, S. Kim and R. Gounder; Consideration of the Aluminum Distribution in Zeolites in Theoretical and Experimental Catalysis Research; ACS Catal. **2018**, 8, 770-784.

3.2. Geometry optimisations of the candidate zeolites. A Table in the Supporting Information shows details about the volume and cell parameters of all the optimised candidate zeolite structures. The geometry optimisations have been performed using GULP software with 25 cycles using the BFGS optimiser plus subsequent 10 cycles using the RFO optimiser^{32 33}. The “comp” (constant pressure) option has been used instead of the “conv” (constant volume) since one of the features of this procedure is to allow new structures to be obtained by expanding or shrinking the original unit cell, hence introducing an additional possibility to relocate atoms in positions of minimum energy using more degrees of freedom, leading to a larger chance of obtaining a stable structure. An analysis of volume variation (between the T-only CIF file given by zeoGAsolver and the geometry optimised) is shown in Table 1, with averages over zeolite structures (avg. zeo) and over force fields (avg. ff).

Table 1. Volume variation (from initial-zeoGAsolver to the geometry optimised) of 28 candidate zeolites. “X” means that the zeolite structure optimisation did not result in a tetracoordinated structure.

Zeolite Codename	BS	force-fields			avg. zeo (%)
		SC	SLC	VLC	
0303_64567	X	28	X	33	30
0310_48918	X	X	X	4	4
0902_181848	X	10	X	17	14
0_30894	X	5	X	3	4
0_34894	-10	-6	-7	6	7
0_44627	-12	-7	-11	-1	8
1_11481	-3	-0	-3	3	2
3_1365021	9	14	11	21	14
3_27767	-3	3	1	9	4
3_31105	X	-18	-20	-5	14
4_15364	-5	-7	-11	6	7
4_76033	-8	X	-7	4	6
4_98439	16	-11	-12	-1	10
5_27095	24	X	-1	9	11
5_51886	X	10	2	15	9
6_18831	X	22	18	29	23
6_45037	X	-13	-8	-4	8
7_31194	X	-23	-28	-9	20
7_5188	X	-9	X	7	8
8_111416	X	-9	-7	0	5
8_33283	-8	-5	-9	2	6
8_46824	13	18	14	X	15
9_13403	22	13	6	17	14
9_25035	X	6	2	14	7
9_28607	X	X	-9	-9	9
9_3540	X	X	4	11	8
9_3746	X	X	X	-8	8
9_42398	-5	3	-1	8	4
avg. ff (%)	11	10	9	7	

Throughout zeolite structures (avg. zeo), variations up to 30% indicate how flexible is the optimisation procedure which allows to find a zeolite significantly different from the initial candidate. These are the cases in which the force field is contributing actively to find a new

³² J. D. Gale; GULP: a computer program for the symmetry adapted simulation of solids; J. Chem. Soc. Faraday Trans. **1997**, 93, 629-637.

³³ J. D. Gale and A. L. Rohl; The General Utility Lattice Program (GULP); Mol. Simul. **2003**, 29, 291-341.

zeolite. In spite of the large fitness, very close to unity, of the original (T-only) structure, the introduction of oxygens, and the geometry optimisation using the force field lead to a more realistic description of the system. An analysis throughout force fields (avg. ff) reveals that, on average, the two core-shell force fields (**SC** and **SLC**) lead to similar values of volume variations (10% and 9%), with **BS** giving a slightly larger volume difference (11%) and **VLC** giving the lowest (7%) average difference between the optimised and the initial volumes. More importantly is to analyse the number of failed optimisations (“X”) with each force field, with **BS** performing poorly (15 failures out of 28 structures), the core-shell force fields (**SC** and **SLC**) showing an intermediate behaviour (6 failures), and **VLC** performing extremely well (1 failure). The success of **VLC** must be assessed to being parameterised for amorphous silica and it is performing particularly well in regions far from the zeolite minima. The bad performance of **BS** is probably due to the presence of two three-body harmonic bonding terms (O-Si-O and Si-O-Si) instead of only one (O-Si-O) in **SLC** and **VLC** force fields. This introduces too much order in the requirements for optimisation and fails if the initial structure is far from the minimum. **SC** force field, also with O-Si-O and Si-O-Si terms performs clearly better than **BS**, by having an anharmonic function to describe the flexible Si-O-Si angle, while the harmonic function in **BS** is less realistic far from the equilibrium.

3.3. Structural and topological analysis of the optimised candidate zeolites. The resulting connectivities and vertex symbols of the candidate zeolites have been compared with those in the IZA database, with 8_46824 giving the same result than CHA, and 9_42398 giving the same result than SOD. In the case of 9_42398, the small cell variation upon optimisation suggests that the finding is done by zeoGAsolver, whilst in the case of 8_46824, the cell variations are 13%-18% depending on the force field, which suggests a significant role of the geometry optimisation process in finding this zeolite. Most structures in Table 2 show the same number of inequivalent T-sites before and after geometry optimisation. Five structures show a reduction in number of inequivalent T-sites (3_31105, 8_111416, 8_46824, 9_3540 and 9_42398), while one structure shows an increase in that number (0310_48918).

The symmetry has also been analysed after the geometry optimisation, although this is a non trivial task. The phonopy software³⁴ has been used with increasingly larger tolerance, from 10^{-4} to 0.02 until a cell different to P1 is obtained (Table 2). The resulting unit cells have in turn been modified by moving the atomic positions according to the maximum tolerance trying to achieve an overlap between symmetry related atoms. Increasingly larger tolerances lead to higher symmetries but in 7 cases cells with P1 symmetry could not be upgraded to a higher symmetry. This far from optimum procedure does not allow to ensure that the symmetry obtained is the largest possible in the corresponding topology. Those cases where the number

³⁴ A. Togo and I. Tanaka; “First principles phonon calculations in materials science”, *Scr. Mater.* **2015**, 108, 1-5.

of inequivalent T-sites after geometry optimisation is lower than in the original cells (3_31105, 8_111416, and 9_3540) should give higher symmetry in the optimised structure than in the original cell, and it is not the case. The correct trend is observed for 8_46824 and 9_42398, where a reduction in the number of inequivalent T-sites leads to an increase in the symmetry.

Table 2 does not indicate which force field(s) succeeded in finding the highest space group for each candidate zeolite. The respective number of findings was 10, 12, 9 and 16 for **BS**, **SC**, **SLC** and **VLC** respectively.

Table 2. Number of inequivalent T-sites and symmetry number of space group of 28 candidate zeolites obtained by zeoGAsolver and the corresponding values after geometry optimisation. The number of T-sites after geometry optimisation has been found by calculating their connectivity sequences. Asterisks indicate structures with changing number of inequivalent T-sites upon geometry optimisation.

Codename	T-sites origin.	T-sites optimi.	Symmetry origin.	Symmetry optimi.
0303_64567	4	4	63	62
0310_48918	4	18*	63	2
0902_181848	4	4	63	63
0_30894	3	3	12	14
0_34894	3	3	12	2
0_44627	3	3	12	1
1_11481	2	2	63	63
3_1365021	2	2	221	221
3_27767	3	3	12	4
3_31105	4	2*	12	2
4_15364	3	3	12	2
4_76033	3	3	12	2
4_98439	4	4	63	51
5_27095	3	3	12	1
5_51886	3	3	12	14
6_18831	2	2	221	221
6_45037	3	3	12	14
7_31194	3	3	12	2
7_5188	3	3	12	1
8_111416	5	4*	12	2
8_33283	3	3	12	12
8_46824	3	1*	12	166
9_13403	2	2	63	63
9_25035	3	3	12	14
9_28607	3	3	12	1
9_3540	3	2*	12	1
9_3746	3	3	12	2
9_42398	3	1*	12	148

3.4. Feasibility of the candidate zeolites. Two criteria for feasibility have been employed to assess the feasibility of the candidate zeolites, the energy and the structural LID criteria based in the study by Li. et al.¹³ described earlier. The results are indicated in Table 3. The energies of α -quartz calculated with each force field are also indicated for the sake of comparison. A justification of feasibility in terms of energetic criteria does not seem possible since there is not a clear trend that can be considered general for all the force fields tested. In order to be applied on a large number of structures, optimisation procedures tend to be simplified, as in

this case with a maximum number of 35 geometry optimisation, which results in some structures still far from the minimum. It could then be suggested that any structure whose geometry optimisation does not fail should be considered as feasible regardless its energy. The second criteria (LID), based on the analysis of local interatomic distances explained above requires the optimisation to be carried out with SLC force field and in order to apply this to all candidate structures, those whose SLC-optimisation failed have been reoptimised using a better starting geometry obtained from a successful optimisation with any other force field. All this process gives 7 feasible zeolites, and 4 zeolites where only one LID-condition fails.

Table 3. Relative energies per SiO₂ unit (kJ/mol) of the structures optimised with the **BS**, **SC**, **SLC** and **VLC** force fields, and feasibility according to the LID-criteria¹³. Feasible structures are indicated as “yes”, and those not feasible are indicated by the number of conditions failed (out of a total of 8). “X” means that the zeolite structure optimisation did not result in a tetracoordinated structure.

Codename	E(BS)	E(SC)	E(SLC)	E(VLC)	LID
0303_64567	X	6	X	2	1
0310_48918	X	X	X	30	3
0902_181848	X	32	X	69	2
0_30894	X	50	X	84	2
0_34894	37	27	31	69	1
0_44627	12	10	16	17	yes
1_11481	21	8	13	0	yes
3_1365021	23	19	25	49	yes
3_27767	26	33	26	45	yes
3_31105	X	43	45	84	4
4_15364	41	27	30	69	1
4_76033	43	X	37	49	4
4_98439	268	19	21	49	yes
5_27095	202	X	25	45	2
5_51886	X	26	30	60	yes
6_18831	X	37	43	67	1
6_45037	X	36	56	62	4
7_31194	X	30	36	85	3
7_5188	X	51	X	101	3
8_111416	X	95	81	116	6
8_33283	43	30	34	68	2
9_13403	144	33	36	54	3
9_25035	X	25	30	60	yes
9_28607	X	X	103	79	4
9_3540	X	X	36	43	3
9_3746	X	X	X	80	2
α-quartz	0	0	0	2	

The 7 candidate zeolites assessed as feasible (0_44627, 1_11481, 3_1365021, 3_27767, 4_98439, 5_51886, 9_25035) are shown in Figure 1. Regarding the channel systems, 3_27767 contains medium size cavities containing 12-rings, each cavity connected by six 8-rings, giving a 3-D channel system. 4_98439 contains a unidimensional straight 10-ring channel connected perpendicularly by short 8-ring channels, giving a 2-D channel system. 5_51886 contains large cavities containing 12-rings connected by 8-rings giving a straight channel system, connected perpendicularly by a small pore channel of elliptic shape. 9_25035

contains an elliptic medium pore channel made by 12-rings not oriented perpendicularly to the channel. This medium pore straight channel is connected perpendicularly through a 8-ring channel, giving a 2-D channel system. 0_44627 contains a 1-D channel system made by sinusoidal 8-rings, 1_11481 is a clathrasil, and 3_1365021 displays a 3-D small pore (8-ring) channels with a very large cube-shape cavity containing as many as 18 intersections.

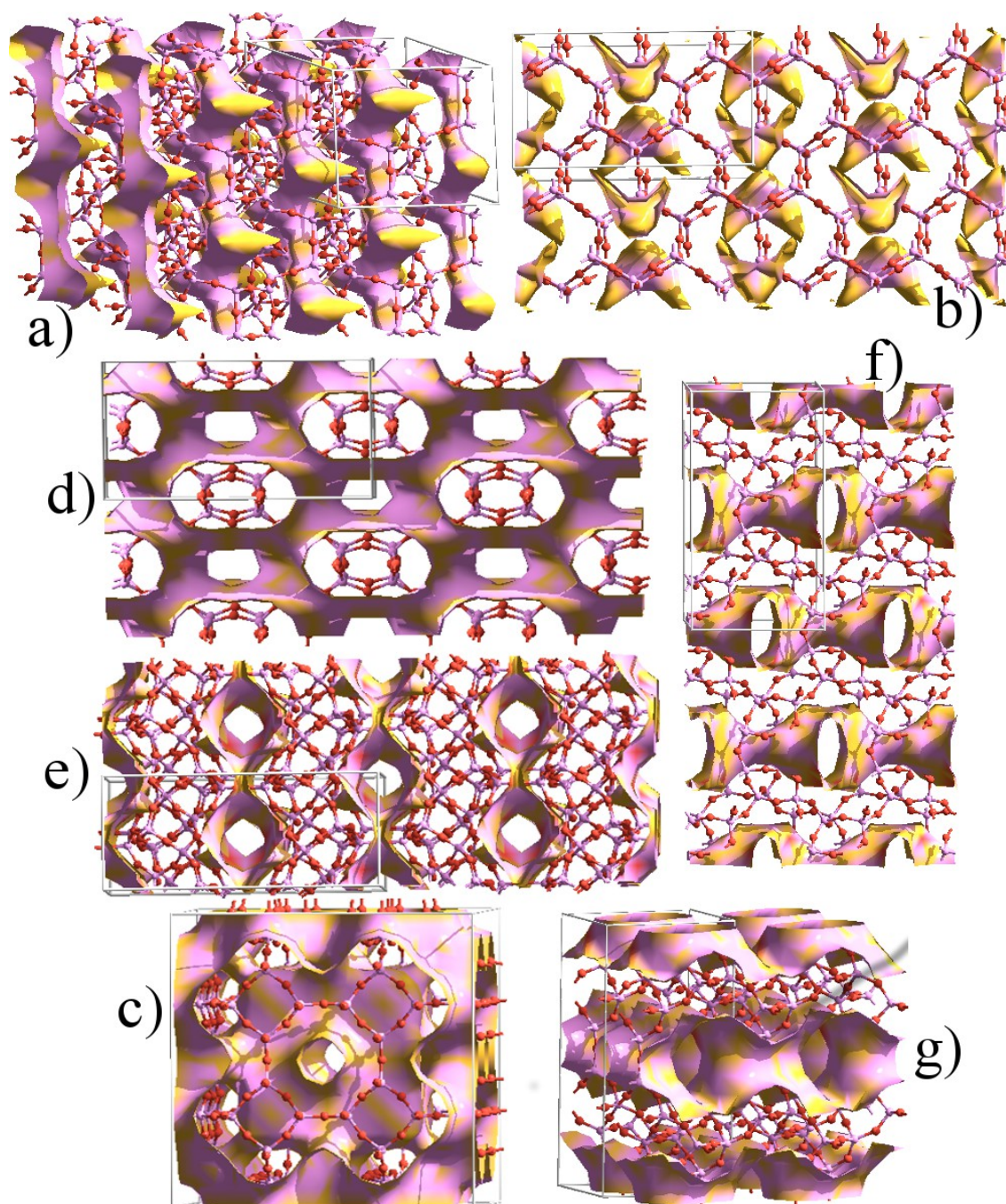


Figure 1. Seven feasible hypothetical zeolites. a) 0_44627; b) 1_11481; c) 3_1365021; d) 3_27767; e) 4_98439; f) 5_51886; g) 9_25035.

4. Conclusions.

A new methodology to perform geometry optimisation on candidate zeolites obtained by a genetic algorithm is proposed. Since the fitness function employed by the genetic algorithm (zeoGAsolver) does not refer to oxygen but only T-atoms, it is perfectly possible, albeit not probable, that structures found with fitness = 1 do not finally correspond to real zeolites due to the absence of evaluation of the effects due to the presence of oxygen atoms. With the aim of, not only testing if the candidate zeolite is stable, but also with the idea of allowing changes in the atomic positions until a stable zeolite is found, an optimisation procedure has been added as a new software to be executed after zeoGAsolver. The software not only introduces the oxygen atoms and makes four parallel unconstrained geometry optimisations using as many force fields, but also it is script-integrated with algorithms to make this automatically for an arbitrarily large number of output files obtained from zeoGAsolver. As a result of testing zeoGAsolver trying to find 11 known zeolites (LTA, NPT, BIK, AFO, AHT, AEI, ATS, CDO, RTH, STF and ITW), 28 candidate zeolites containing 4-rings as the smallest have been found after the automated geometry optimisation using force fields. Using criteria based on structure and energetics, a short list of seven feasible hypothetical zeolites is proposed. The present algorithms are being updated in order to be able to tackle more complex zeolites (containing more than four inequivalent T-sites) in a reasonable CPU time.

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