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Analysis of x-ray diffraction data using a hybrid stochastic optimization method

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Abstract

An hybrid optimization procedure based on two stochastic algorithms, a genetic algorithm and simulated annealing, is proposed and applied to the problem of extracting a crystal configuration from grazing incidence x-ray diffraction data. Problems like this, with many parameters and very complex fitness landscapes, can be optimized by running a genetic algorithm and then refining the search with a simulated annealing procedure. A case study of finding the structure of a self-assembled monolayer of *n*-alkyl thiols ($n = 10$) on the (111) surface of gold is reported.

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1. Introduction

The understanding of conformational properties of organic molecules, native structures in protein folding, minimum potential energies in atomic clusters or, in general, complex multi-parameter optimization problems encountered while testing theories against experiments, are today subjects of considerable interest. Very often these difficult problems are intractable because deterministic optimization algorithms get trapped on a local minimum. Most methods adapt the so far best solution in the direction in which this current solution is improved and the algorithm stops when no more improvement is observed. In practice, however, one most likely gets a sub-optimal solution. The ability to circumvent such local minima and keep improving the solution toward the global minimum is the goal of current study.

Beyond the classical deterministic methods that are based on the calculation of the derivative at the current position (gradient method) or the performance of trial steps (simplex optimization), elegant and new methods, based on the diffusion equation [1], quantum annealing [2], relaxation of lattice structures [3], etc, have been proposed to solve hard optimization problems. But when the complexity of the problem is high, the failure of these deterministic methods in finding global minima is the usual result.

Blind-search stochastic techniques, based on the analogy with natural phenomena, have also been proposed to solve hard problems in chemistry and physics. The two best-known techniques are simulated annealing [4] and genetic algorithms [5, 6]. Genetic algorithms (GA), as global optimization procedures, can be used in both discrete as well as continuous problems. They search efficiently in different regions of the space of solutions and, even if they get trapped on a local minimum, they can also escape from them. GAs are based on the concept of the survival of the fittest: a population of individuals is created using genetic operators, the fittest individuals in a given generation survive and reproduce in the next generation. The process of creating new generations, through crossover and mutation operators, is repeated until some stop criterion is satisfied (quality of solution, number of generations or computer time used). The simulated annealing (SA) strategy, on the other hand, mimics the slow cooling of matter as it evolves towards a low-energy crystal structure. The SA algorithm functions as follows: taking one solution, a new solution is generated; if the new solution is of better quality, it is accepted, otherwise the new solution is accepted according to a probability that depends on the current temperature of the system and an equilibrium requirement. Thereafter, the temperature is decreased according to a cooling schedule, seeking equilibrium in every step. At high temperatures the SA algorithm explores a greater region of the feasible space; as the temperature decreases, the algorithm searches smaller and smaller regions of the feasible space and eventually converges to an optimal solution.

Although many difficult optimization problems have been solved by using either GA or SA, it would not be wise to affirm that one of these stochastic algorithms is better than the other. Indeed, the success of a stochastic method often depends on the experience of the user and the problem itself. On one hand, GA are excellent at finding the neighbourhood of the global solution, although due to the inherent discrete nature of the algorithm, that solution is rarely obtained. Perhaps the best attribute of GA is what many deterministic methods lack most: the starting solutions are random and are not necessarily in the vicinity of the wanted one. This is an important feature if one does not know *a priori* where the optimal solution in the feasible space is found. On the other hand, avoiding premature convergence, due to accepting with some probability a worse solution, is a good attribute of SA. If used properly, SA can also be an effective global optimization algorithm, and most importantly, SA excels in doing refined searches inside prominent regions. But once more, the algorithm might get trapped on local solutions when the problem has a great complexity.

The idea of hybridizing methods in order to strengthen the weaknesses of some algorithms, has been around in the literature for a long time. This hybridization can be deterministic–deterministic, stochastic–deterministic and stochastic–stochastic. The literature abounds with the first ones (see [9]) and more recently with the others [7, 8].

In this paper, we propose a hybrid optimization method based on GA and SA. Then we apply this method to the very complex problem of finding the structure of a self-assembled monolayer of *n*-alkyl thiols ($n = 10$) on the (111) surface of gold. This problem has considerable importance in today's technology as a model system to understand supramolecular assembly and wetting [10].

In section 2, we describe the basic elements of the algorithm and write the pseudocodes of our GA and SA. In section 3, we explain briefly the principles of x-ray diffraction at low incident angles and write the important formulae used to construct the fitness function. Results and discussions are presented in section 4 and finally some conclusions are drawn in section 5.

2. Description of the method

2.1. Genetic algorithm

The pseudocode for our genetic algorithm is as follows:

```

GENERATE a population of parameter vectors:
   $P(t = 0) = \{\mathbf{x} = (x_1, x_2, x_3, \dots, x_N)\}(t = 0)$ 
  each vector of parameters is analogous to a chromosome.
EVALUATE  $E(\mathbf{x})$  for each member of the population  $P(t)$ 
  ( $E$  is a fitness function of the  $N$  parameters:  $\mathbf{x} = (x_1, x_2, x_3, \dots, x_N)$  to
  be optimized), select the best members of the population accordingly.
WHILE (termination condition is not met)
   $t = t + 1$ 
  GENERATE through SELECTION a new population of parameter
  vectors  $P(t) = \{\mathbf{x} = (x_1, x_2, x_3, \dots, x_N)\}(t)$  out of  $P(t - 1)$ 
  APPLY CROSSOVER to the member's chromosomes of  $P(t - 1)$ 
  according to crossover probability
  APPLY MUTATION to the new chromosomes formed according
  to mutation probability
  EVALUATE  $E(\mathbf{x})$  for each member of the population  $P(t)$ 
END WHILE

```

Some important concepts of the above procedure are the following:

- *Representation.* The algorithm must manage a number of N floating point numbers, grouped into a parameter vector. There are basically two options: a binary and a floating point representation. The most popular binary representation is the one proposed by Holland [5], in which chromosomes are strings of mN bytes (zeros and ones), m bytes per parameter. In Holland's chromosome structure there is a semantic difference between this kind of string codification and the real codification of the problem. A floating point representation often works better for continuous optimization problems [16, 17] and is the one we use. In this kind of representation the chromosomes are directly the parameter vectors, thus the length of the chromosomes, N , is m times shorter in this representation than in the binary one, yielding an easier chromosome manipulation and better computational times: a suitable size for the population is determined by the length of the chromosomes and the fact that handling a large population slows down the algorithm.
- *Population initialization.* The population is formed by a certain number of individuals. Each individual is a vector parameter of N components, each parameter of each individual is initialized with a uniform random number between the lower and upper limits of the parameter. This was repeated with all the members of the population.
- *Fitness function.* The fitness function is determined by the function $E(\mathbf{x})$ to be minimized; the lower the value of $E(\mathbf{x})$, the fitter the individual \mathbf{x} .
- *Selection scheme.* We apply the tournament selection scheme as follows: we randomly select three different individuals and select the fittest. We implement an elitist strategy in which the best individual of a generation is copied directly to the next generation.
- *Genetic operators.* The most used genetic operators are crossover and mutation operators. In this work we use two types of crossover operators:
 - (a) Cross1: The offspring are formed through the juxtaposition of parameters of both parents.

(b) Cross2: The offspring are formed using a linear crossover based on the arithmetic combination of corresponding parents using one of the following formulae (the choice between the three being randomly made):

$$Parameter_i = (Parent1.Parameter_i + Parent2.Parameter_i)/2; \text{ or}$$

$$Parameter_i = (n * Parent1.Parameter_i - Parent2.Parameter_i)/2; \text{ or}$$

$$Parameter_i = (-Parent1.Parameter_i + n * Parent2.Parameter_i)/2.$$

The first of these formulae gives simply the middle point between $Parent1.Parameter_i$ and $Parent2.Parameter_i$, the second and third give points closer to the parameters of one parent or the other. This linear crossover produces enough diversity but is not so disruptive as Cross1.

The mutation operator modifies only one parameter for each individual mutated. The modification is made through one of the following formulae:

$$Parameter_i = Parameter_i + Size_i * RandomNumber; \text{ or}$$

$$Parameter_i = Parameter_i - Size_i * RandomNumber.$$

$Parameter_i$ stands for the i th parameter, $Size_i$ stands for the pre-specified size of the modification for the i th parameter, and integer $RandomNumber$ is between 1 and 20. If the value of $Parameter_i$ is smaller (greater) than the lower (upper) limit we adjust the value to the lower (upper) limit.

- *Probability of applying genetic operators.* The probability of making a crossover is unity, but half of the crossovers are made following the Cross1 rule and the other half following Cross2. Trial and error is always needed to choose an adequate mutation probability.
- *Stop criterion.* We stop after a given number of populations has been generated or after the fitness function has converged to a value that may be a minimum. If no convergence is achieved with the given number of populations, the algorithm can restart from the last generation.

2.2. Simulated annealing

The basic pseudocode for the simulated annealing algorithm is:

```

k = 0
u = initialsolution
t = initialtemperature
WHILE termination condition
  WHILE fixed-temperature condition
    v = Perturb(u)
    if ( $f(v) \leq f(u)$ ) or  $random[0, 1] < e^{-(f(v)-f(u))/c_k}$ 
      then u = v
  END WHILE
  k = k + 1
  t = t *  $\alpha$ 
END WHILE

```

The main concepts of the algorithm are defined as follows:

- *Initial temperature.* A very low initial temperature is used in order to make the algorithm more localized and speed convergence to an optimal point in the space of solutions.
- *Condition of repetition at a fixed temperature.* This condition was controlled considering the number of perturbations made and the number of accepted perturbations.
- *The perturbation function.* The perturbation function is the same as the one used for the GA mutation operator.

- *The rate for lowering the temperature.* We define a low rate of 0.50 in order to have a low consumption of time during the SA phase and to promote fine tuning (local search) rather than exploration (extended search).
- *The criterion for termination.* This criterion takes into account the current temperature. When this temperature takes a pre-determined value the algorithm ends. The minimum temperature used was 0.05.
- The energy function is defined as the function to be minimized.

2.3. GA and SA integration

The coupling of the simulated annealing and the genetic algorithm was done in such a way that the GA creates a complete generation (using selection, crossover and mutation). Thereafter, the simulated annealing algorithm is run in order to do a local search to improve a subset of the best individuals. Then we run the GA again and so on.

This particular coupling hopefully takes advantage of the best of each of the two algorithms. On one hand, the GA is an excellent approach to exploring the search space, but has a slow rate of convergence to an optimal solution. The simulated annealing is an excellent option to fine tune the GA solution set in an efficient manner. It should be emphasized that in the problem studied here, neither GA nor SA alone find optimum solutions.

3. A study case

The hybrid optimization method presented above, has been used to look for crystal structures compatible with experimental data of grazing incidence x-ray diffraction from $\text{CH}_3(\text{CH}_2)_9\text{SH}$ self assembled on the (111) surface of gold. The experimental study was performed by Fenter *et al* [10]. Based on the experimental data and following a fitting procedure, it was found that a monolayer structure which consists of a nearly hexagonal two-dimensional arrangement of the hydrocarbon chains with a dimerization of the sulfur head groups, accommodated through a gauche bond, was quite compatible with the experimental results (hereafter we will call the structure proposed by Fenter *et al*, Fenter's disulfide structure, or Fds). The possibility of dimerization of the thiolates was, at the time of presentation of the x-ray diffraction study, contrary to the accepted picture of thiolate bonding structure [11–14]. A later experimental study on the system [15], this time using x-ray standing waves, did not confirm the dimer structure proposed nor did it contradict the dimerization model either. The possibility of finding another geometry compatible with the grazing incidence x-ray diffraction data obtained by Fenter *et al* has thus been opened and our hybrid optimization method has been used on this difficult multiparameter optimization problem.

3.1. X-ray diffraction theory

It is well known from basic diffraction theory [18, 19] that the amplitude, A_a , of a wave diffracted by a single atom at \mathbf{r} , with an electronic distribution function $\rho(\mathbf{r}')$ around \mathbf{r} , can be calculated in the Born approximation by summing the contributions of all the electrons in the atoms:

$$A_a \propto \int d^3\mathbf{r}' e^{i\mathbf{q}\cdot(\mathbf{r}+\mathbf{r}')} \rho(\mathbf{r}') = f(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} \quad (1)$$

\mathbf{q} being the momentum transfer $\mathbf{k}_f - \mathbf{k}_i$ where \mathbf{k}_i (\mathbf{k}_f) corresponds to the incident (final) wave vector. Hence, the atomic form factor $f(\mathbf{q})$ is defined as the Fourier transform of the electronic density $\rho(\mathbf{r}')$. The atomic form factor is well known for most stable elements [20].

The amplitude of the wave diffracted by a unit cell of a crystal of N_c atoms will then be

$$A_c \propto \sum_{j=1}^{N_c} f_j(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}_j} e^{-\frac{1}{6}\langle u_j^2 \rangle q^2} = F(\mathbf{q}) \quad (2)$$

which defines the structure factor $F(\mathbf{q})$, where Debye–Waller factors for the thermal motion of each of the N_c atoms have been included, $\langle u_j^2 \rangle$ being the mean square displacement of the j th molecule.

It is then the electronic density that produces the diffraction signal, and therefore, this is the important quantity to pursue, since it gives us complete information on the associated structure we are interested in studying. What we observe, however, is the diffraction intensity which is directly proportional to the squared amplitude on the diffracted wave, thus the electronic density of the material cannot be deduced simply by an inverse Fourier transform of the diffraction intensity. We circumvent the problem of finding the electronic density by a trial and error method in which a crystal structure, with its corresponding electronic density map, is proposed and theoretical diffracted intensities are calculated and compared with experimental ones. An error function is defined to compare calculated versus experimental diffraction intensities and the crystal structure is adjusted until a—hopefully global—minimum of the function is obtained.

3.2. The fitting procedure

We have defined the error function as follows:

$$E(x) = S\chi^2(x) = \frac{1}{n} \sum_z \sum_i \left(\frac{\xi v_i(q_z, \mathbf{x}) - w_i(q_z)}{\sigma_i(q_z)} \right)^2 \quad (3)$$

where $v_i(q_z, \mathbf{x})$ is equal to $|F^{\text{calc}}(h^i, k^i, q_z)|^2$ for the crystal defined by the parameter vector \mathbf{x} , and $w_i(q_z)$ is the experimental intensity corresponding to the diffracted (h^i, k^i) peak at q_z , which is proportional to $|F^{\text{exp}}(h^i, k^i, q_z)|^2$, ξ is a scale factor chosen to minimize $S\chi^2$, $\sigma_i(q_z)$ is the statistical uncertainty in the experimental intensity $w_i(q_z)$ and the sums are over the n experimental data points. The problem in fitting the diffraction data is to find the parameter vector $\mathbf{x} = (x_1, x_2, x_3, \dots, x_N)$ which defines the crystal structure that minimizes $S\chi^2$. To this end, one proposes at the beginning an initial or reference structure which contains the atoms and molecules thought to be found in a single two-dimensional unit cell. This structure is fed to the algorithm and the algorithm, stochastically but guided by its rules, modifies the structure according to its N degrees of freedom. These degrees of freedom may include: (a) translations and rotations of molecules as rigid bodies, (b) translations of single atoms and (c) change in thermal vibration amplitudes. The distortions or modifications are applied to the reference structure parametrically through N parameters of modification: $x_1, x_2, x_3, \dots, x_N$.

We have defined the reference structure by a unit cell of three layers of gold atoms and four thiol radicals $\text{CH}_3(\text{CH}_2)_9\text{S}$, with 12 atoms of gold per layer. The reference structure, along with the parametrization of modifications and the intervals within which each modification parameter can vary, must ensure that all physically plausible structures (monolayer structures of $c(4 \times 2)$ symmetry and hexagonal symmetry) have been included in the set of structures which are being tested.

The definition of the reference structure and the parametrized modifications to it have been taken according to the already presented qualitative analysis of the experimental diffraction data [10], and following the consistent-structure search performed by the cited authors. The

Table 1. Characteristics of several representative optimized structures. The type 4g stands for a 4-gauche structure, 2t2g stands for a 2-all-trans + 2-gauche structure and 4t refers to a 4-all-trans structure; the error function is $S\chi^2$; θ is the tilt angle (in degrees) with respect to the surface normal and $90^\circ - \phi$ is the orientation of the tilt with respect to the next nearest neighbour direction; X–Y is the minimum distance (in Å) between atoms X and Y and $(X–Y)_z$ is the distance projected to the surface normal, i.e. the vertical distance; $(C–C)_z$ refers to the last carbons of inequivalent chains.

Label	Type	$S\chi^2$	θ	ϕ	S–S	S–Au	C–Au	$(S–S)_z$	$(S–Au)_z$	$(C–C)_z$
A	4g	1.8	39	74	2.3	2.5	2.2	1.5	2.1	0.1
B	4g	1.8	38	81	3.5	2.5	1.9	1.9	2.1	2.5
C	4g	2.1	34	74	2.7	2.8	2.0	1.3	2.7	2.2
D	4g	2.1	33	70	2.1	2.9	3.0	1.0	2.6	0.2
E	2t2g	2.6	29	71	3.5	2.3	2.3	0.6	2.1	1.4
F	2t2g	2.6	27	47	4.8	2.3	2.4	0.8	2.1	1.4
G	4t	5.7	33	63	4.0	2.4	3.1	0.2	2.1	0
H	4g	1.7	37	69	2.3	2.2	2.3	0	2.0	0.1
I	4g	1.4	50	23	2.5	1.7	1.5	0.2	1.6	0.3

modifications to the structure include: the variation in the position of the radicals which allows (but does not force) them to get close enough to be considered dimerized; variation of the tilt angle; tilt direction and twist about the hydrocarbon chain axis of the thiol radicals; lateral relaxation of the first gold layer and vertical relaxation of the first two gold layers. Furthermore, we have included the S–S vertical distance and the thermal vibration amplitude as parameters; all these, plus the overall scale, give a total of 43 parameters to fit. The complete set of parameters specified for the system, represented by the vector \boldsymbol{x} of dimension N , is the driving force that makes the structure evolve to the one that hopefully produces the measured diffraction data.

We have explored three different possibilities for the crystal structure, two included in the search by Fenter *et al.*: one corresponding to a structure in which the thiol radicals have an all-trans configuration (4-all-trans) and another in which the radicals present a gauche in the S–C bond (4-gauche); the third case, not explored before, considers the possibility of having two all-trans radicals and two gauche radicals in the unit cell (2t2g). Let us remark that we have not, in any way, forced the formation of dimers.

The value used for n in Cross2 was 3 (values greater than 3 create more diversity than needed, increasing the time of convergence, values smaller than 3 reduce the time of convergence but optimum solutions are more difficult to find). We apply the mutation operator to a small subset (around 10 per cent) of the individuals and for each individual only one parameter is modified. Let us mention that this small value for the mutation probability was due to the fact that the crossover already produced enough diversity in the population.

The size of the population used in this study was 200.

4. Results

Our results have been summarized in table 1 where we present the characteristics of several representative optimized structures obtained by our method. Fenter's disulfide structure (H) is included for comparison, as well as structure I, which is not acceptable because of the small interatomic distances but which shows the algorithm is able to find solutions with smaller error function. Figures 1 and 2 show the experimental diffraction intensities along with the

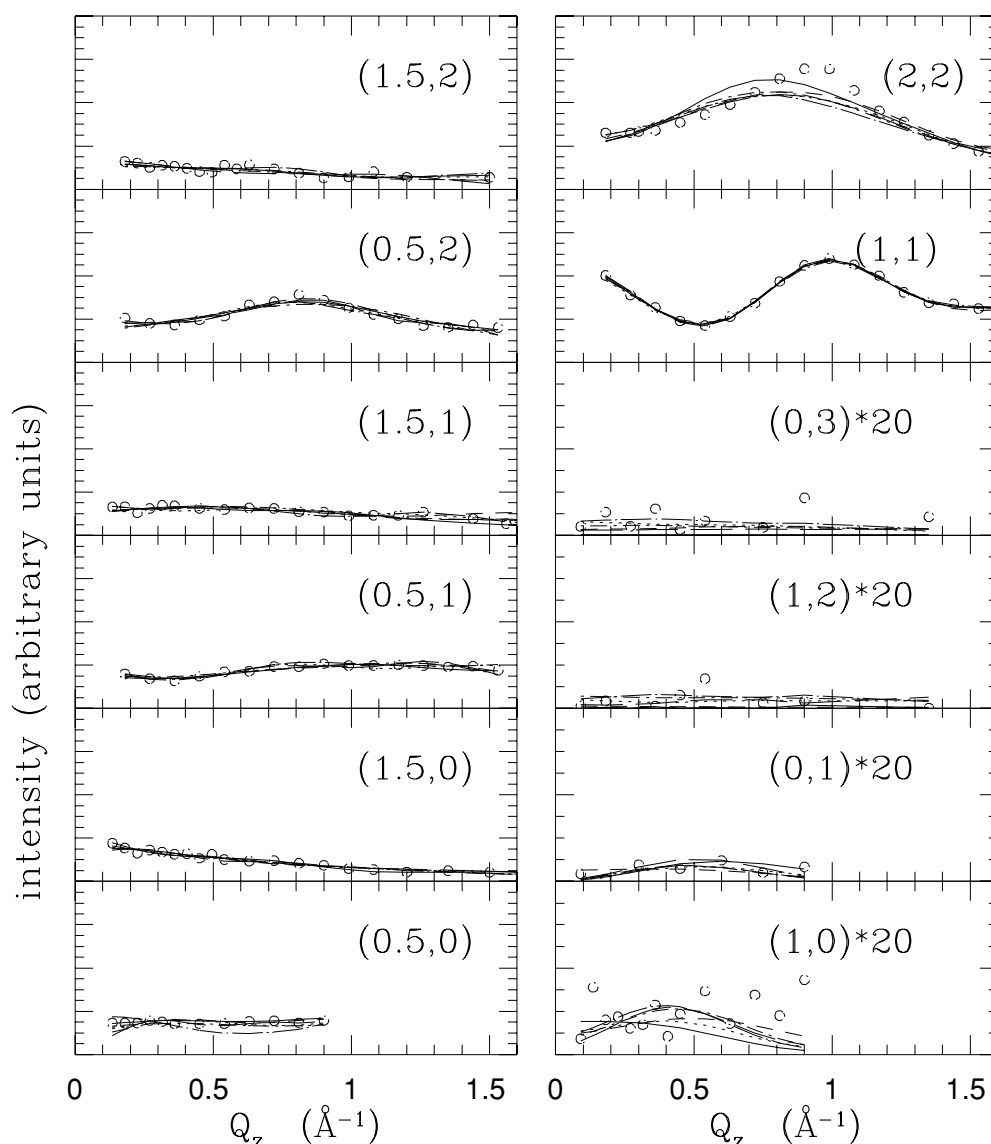


Figure 1. Calculated diffraction intensities of the Bragg rods as a function of Q_z corresponding to structures A, B, C and D. The circles represent the experimental data. The calculated intensities corresponding to Fenter's disulfide structure (structure H) are plotted for comparison (continuous line). The lines of intensity corresponding to different structures are so close together that it is difficult to differentiate one from another, except for the continuous line in the (2, 2) peak. The purpose of this figure is to show how good the fit is for the 4-gauche structures.

calculated intensities corresponding to the optimized structures (in figure 1 for structures H, A, B, C and D and in figure 2 for structures H, E, F, G and I). The calculated intensities corresponding to Fds (structure H) are plotted in each figure for comparison (solid lines). It can be noted that most of the diffraction peaks are well fitted for all the structures, the main exceptions being the (0.5, 2) peak and more remarkably, the (2, 2) peak for the 2t2g and

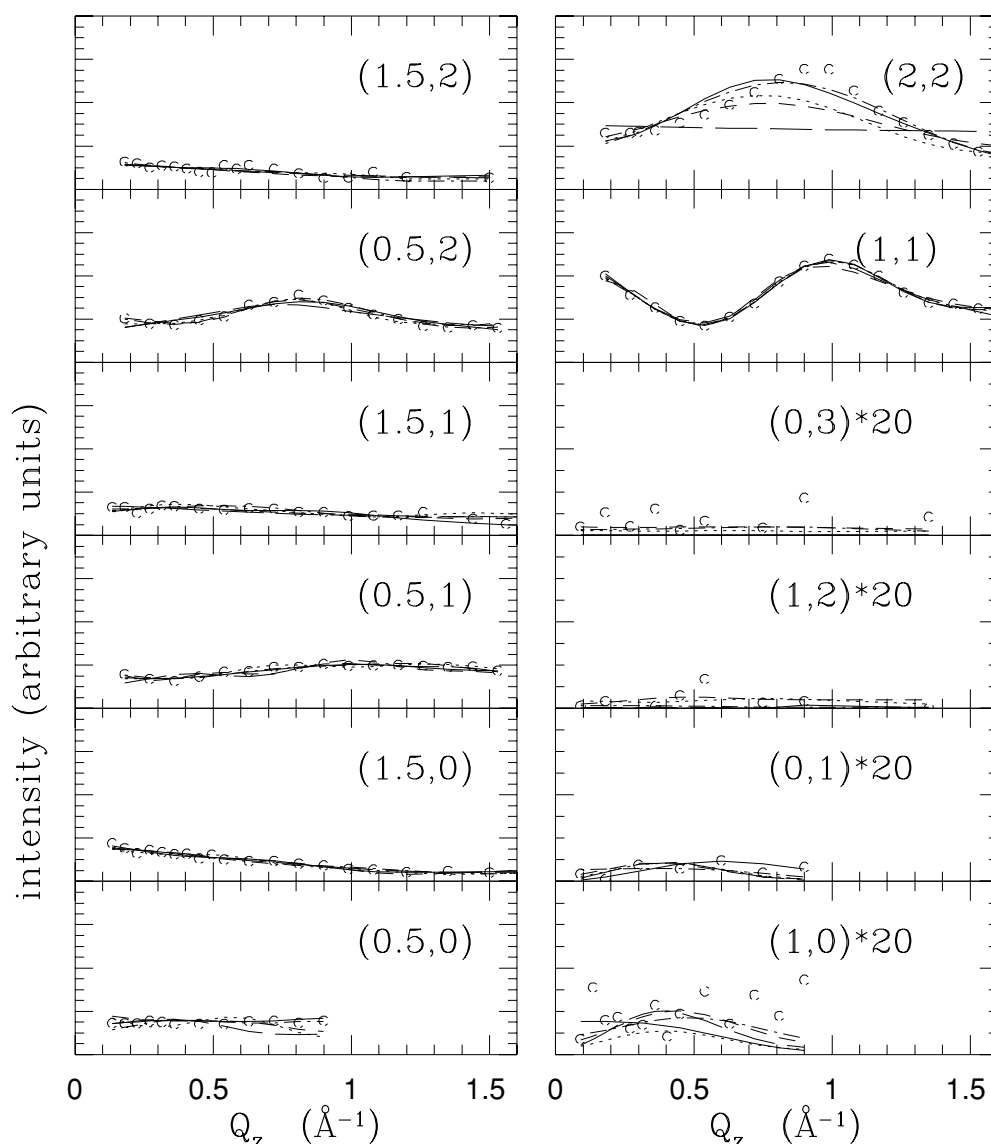


Figure 2. Calculated diffraction intensities of the Bragg rods as a function of Q_z corresponding to structures E, F, G and I. The circles represent the experimental data. The calculated intensities corresponding to Fenter's disulfide structure (structure H) are plotted for comparison (continuous line). Again, the lines of intensity corresponding to different structures are quite close, except for the (2,2) peak, in which we get a flat intensity for the 4-trans structure (G); the line that goes together with the continuous line corresponds to structure I and the lines in between correspond to structures E and F. 4-trans structures cannot fit to this peak.

4-all-trans structures, the latter yielding a flat signal, i.e. a diffraction peak (surface Bragg rod) with no Q_z dependence.

Some interesting features may be noted:

- For the case in which the thiol radicals have an all-trans configuration we have obtained a fit with a minimum $S\chi^2$ of 5.7, which is better than the best fit obtained by Fenter *et al*

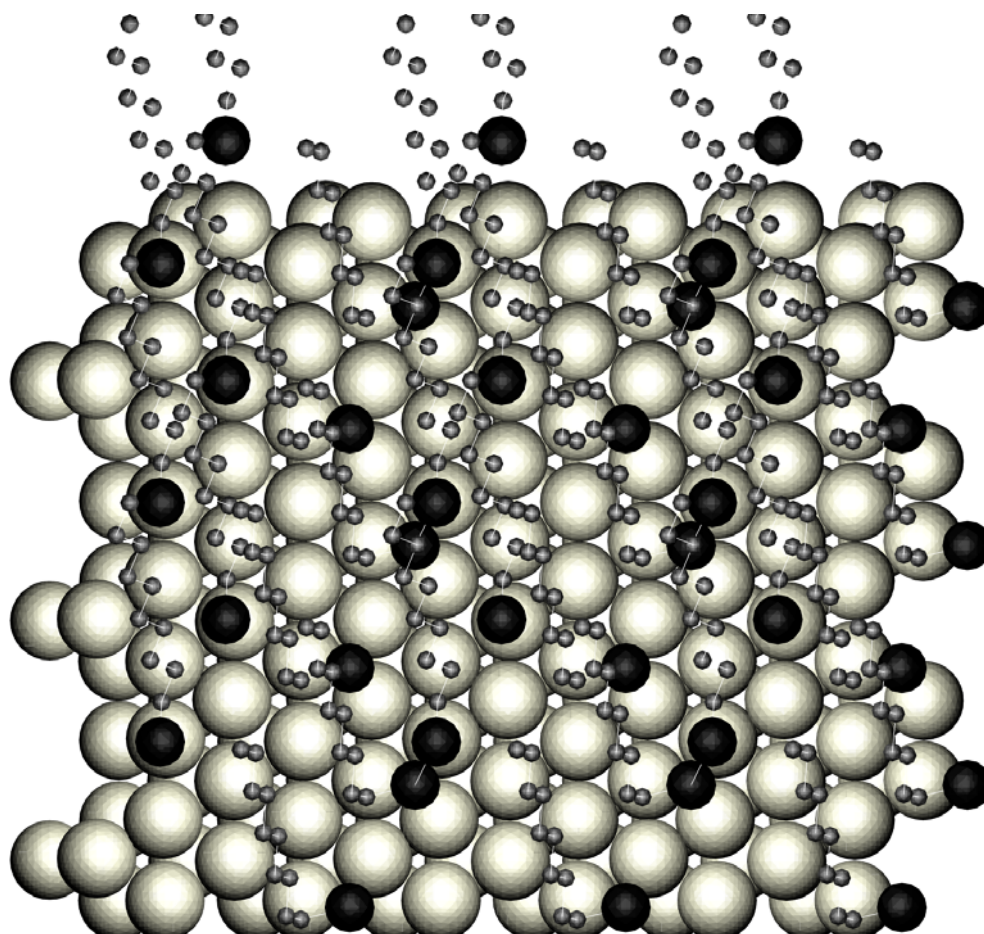


Figure 3. Schematic top view of structure A. The large spheres represent the gold atoms, the dark ones represent the sulphur atoms and the small ones represent carbon.

for a 4-all-trans structure ($S\chi^2 = 16$), but still poor compared with the fit achieved for the other structures.

- For the other cases in which 2 or 4 thiol radicals have a gauche in the S–C bond, we have obtained several structures whose fit is as good as the fit corresponding to Fds.
- We have been able to arrive at Fds only when we introduced in the initial population of parameter vectors \boldsymbol{x} , a vector that defines a similar structure. No other structure with all radicals dimerized has been found.
- We have found several structures, for instance A and D, where radicals coexist with disulfides: two radicals per disulfide. A schematic of structure A is shown in figure 3. Other structures, such as B and C, present a minimum S–S distance much smaller than the 5 Å expected in the hexagonal ($\sqrt{3} \times \sqrt{3}R30^\circ$) structure but larger than the S–S dimer bond. A schematic of structure B is shown in figure 4. Starting from random parameters most of the times, the 4-gauche structure evolves to one of the latter kind.
- We have also found a good fit with the experimental data, although it is not one of the best fits, for a structure (F) where the sulfurs form a nearly $\sqrt{3} \times \sqrt{3}R30^\circ$ lattice. However, it is important to note that in spite of the spatial array of the sulfur atoms, the overall

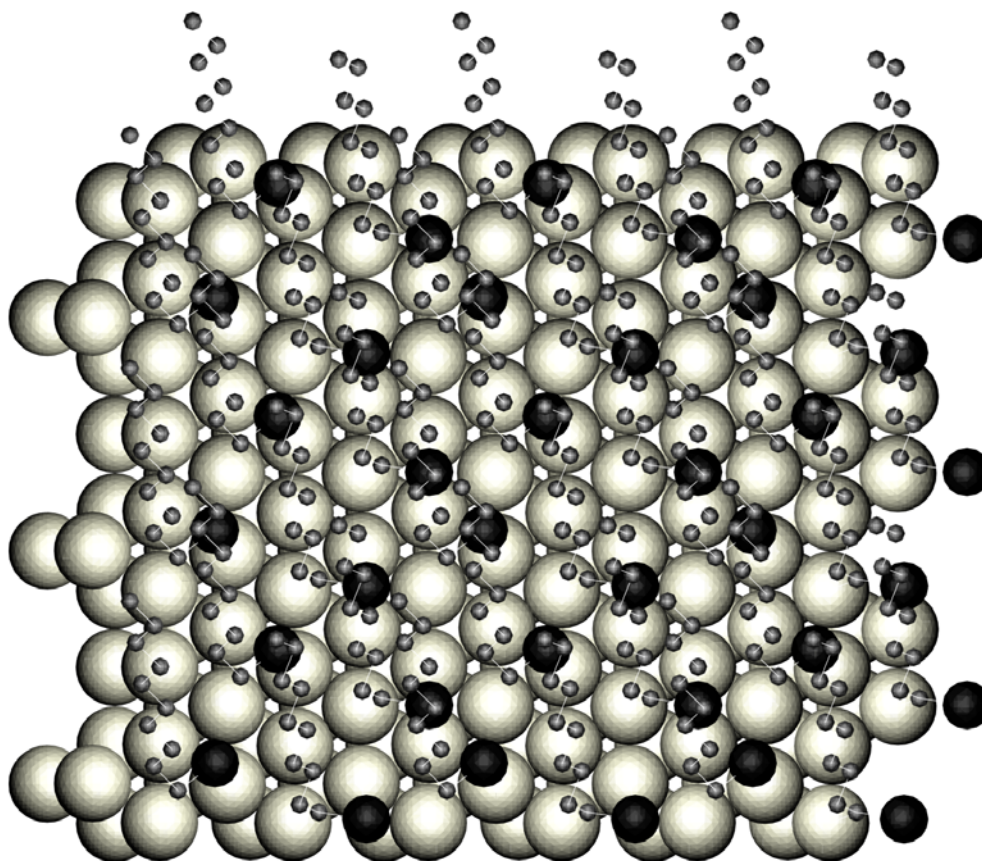


Figure 4. Schematic top view of structure B. The large spheres represent the gold atoms, the dark ones represent the sulphur atoms and the small ones represent the carbons.

periodicity of this structure is that of a $c(4 \times 2)$ cell due to the structural and orientational differences of the adsorbed molecules.

- A feature always present in a good fit is the nearly hexagonal two-dimensional arrangement of the hydrocarbon chains, and for the 4-gauche structures, the tilt and orientation of the chains are quite similar to those of Fds. Less constant are the vertical distance between sulfurs and that between the last carbons in the chains of inequivalent molecules (see table 1).

Summarizing, we have found several crystal structures of a monolayer of $\text{CH}_3(\text{CH}_2)_9\text{SH}$ self-assembled on the (111) surface of gold, compatible with experimental x-ray diffraction data. Some of the optimized structures do not present dimerization of the adsorbed molecules. The several optimized structures should be tested against other experimental evidence such as x-ray standing waves [15], or may be used as starting points for theoretical calculations such as first principles calculations of bonding energy to further test the dimerization hypothesis.

5. Conclusions

A stochastic search procedure based on a genetic algorithm and simulated annealing has been proposed to solve complex fitting problems. The method combines the searching abilities

of a genetic algorithm and simulated annealing to find correct and optimized solutions. The method is robust and does not need to be fed, at the starting point of the searching procedure, with solutions already close to physically optimal ones as in the gradient method. The local search around promising regions in the landscape of solutions is carried out by the simulated annealing algorithm. Although one cannot state that a global optimum has been found, the refinement made by the simulated annealing method greatly improves the solutions compared to those obtained only by GA (not reported here).

The method proposed was applied to a grazing incidence x-ray diffraction problem that involved more than 40 parameters and from the several optimized solutions obtained; an important fact was made clear: several different structures may be compatible with grazing incidence x-ray diffraction experimental data; it is necessary then, that this experimental technique be complemented with other experimental techniques if the geometrical structure of a system is to be determined. The consequences of this conclusion should be explored in future studies. The software written by us and used in this work is available at: <http://campus.mor.itesm.mx/jtorres/GASA/>.

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