

MARVIN: A new computer code for studying surfaces and interfaces

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1 Overview

Inorganic surfaces and their interaction with molecules play a significant role in a wide range of processes such as catalysis, crystal growth, corrosion and electrolysis. Only limited experimental information on the detailed structure of inorganic surfaces is available. Therefore, atomistic simulations can help us to understand the details of surface chemistry. It is this void that **MARVIN'S PROGRAM** (Minimisation And Relaxation of Vacancies and Interstitials for Neutral Surfaces, Program) or **MARVIN** is designed to fill.

To date, **MARVIN** has been applied to many types of surface simulation problems. A few of these problems include surface structure and crystal morphology, [1] the atomic force microscopy (AFM) imaging process, [2] and the structure of small clusters on surfaces [3].

MARVIN is not a program that uses new techniques, but a new program incorporating the ideas and formalisms of both **MIDAS** [4] and organic molecular mechanics modelling. The techniques used in **MIDAS** have been expanded to include more potential types and the concept of molecules and connectivity. These control the building of crystals and the specifying of potentials, the result of which is a more flexible program that allows not only the modelling of simple inorganic surfaces and their interfaces but also the surfaces of molecular and molecular ionic systems and the docking of molecules and ions.

2 Features

As in **MIDAS**, the foundation of **MARVIN** is a "full" 2-dimensional Ewald sum [5]. The short-range two-body interactions can be represented with the following functional forms: Lennard-Jones, Buckingham, Morse, harmonic, cubic spline, and coulomb-subtract. These can also be used in arbitrary combinations. The harmonic three-body bond bending and four-body torsion terms are also included for modelling silicates, molecular solids and organic molecules adsorbed on surfaces.

Currently, two different minimisers have been implemented in **MARVIN**, conjugate-gradient and BFGS [6]. The convergence properties of these minimisers is complementary. Conjugate-gradient

works very well for large numbers of atoms and high gradients, while BFGS works better when the gradient is lower.

The program **MARVIN** was written in “C”, to take advantage of three key features of the language. The first reason is that dynamic memory allocation routines are standardised in “C”. This allows the program to allocate memory as it needs it and eliminates the need to recompile the program when the problem size increases. Also, “C” allows for data abstraction, for example structures and unions. This helps to create a cleaner program, with groupings of related parameters. The final reason, is the ease of writing an input parser that allows for a “user friendly” input file.

3 Methodology

Currently, **MARVIN** can perform energy minimisation of surfaces, interfaces and surfaces with molecules (small clusters, AFM tips) adsorbed near them. The program is limited to neutral defects because of the 2 dimensional periodicity. As mentioned earlier, the electrostatic contribution is computed with an Ewald sum. The short-range potentials are also computed with a lattice sum instead of using “minimum image”.

The energy minimisation is performed for a 2 dimensional cell that is divided into two regions (see Figure 1). The two regions are called *region 1* and *region 2*. The atoms in region 1 are allowed to relax to minimise the total energy. While the region 2 atoms are fixed to reproduce the effect of the bulk crystal. The total energy is defined as the energy of region 1 embedded in a crystal composed of lattice repeats of itself and region 2.

Along with the total energy, **MARVIN** also calculates the surface energy, and the attachment energy before and after relaxation. The *surface energy* is the energy required to cleave the crystal. The *attachment energy* is the energy released when a “growth slice” is attached to the surface. The effects of relaxation on these quantities are significant and can be quite dramatic.

4 Application: α -quartz

An example application of **MARVIN** is α -quartz. The surface of quartz has to be terminated with hydroxides to fill the bonds broken by cleaving the surface. The resulting *growth morphology* is shown in figure 2, resembles very closely the observed crystal. More details about these calculations will be published soon [7]. The equilibrium morphology for α -quartz system exhibits the systematic problem of equilibrium morphologies. This problem is the appearance of high index faces due to the large reduction of surface energy during the minimisation procedure. The result of this surface energy reduction is that the morphology becomes spherical. This problem has yet to be explained [8].

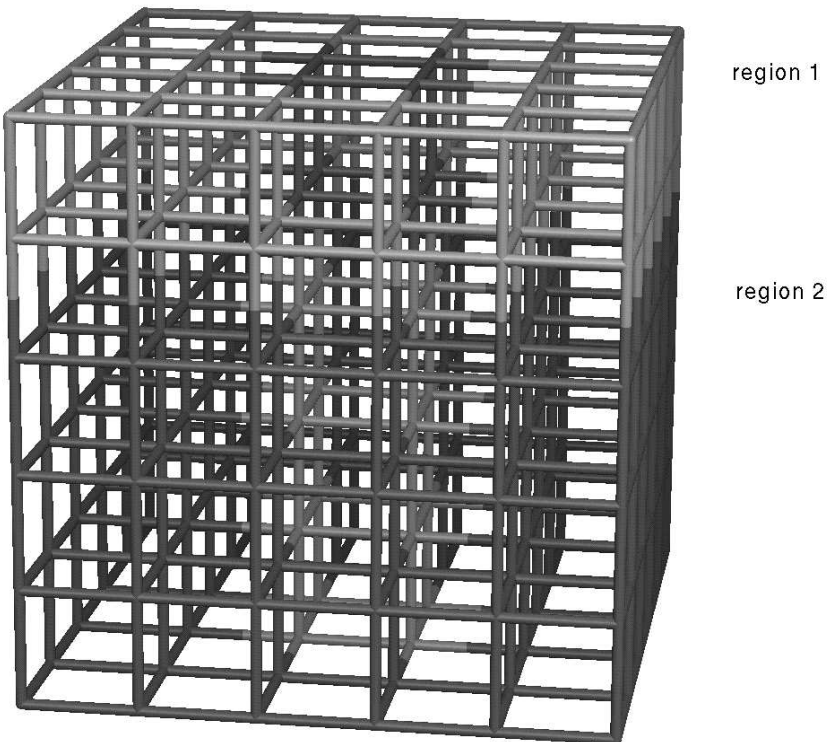


Figure 1: MgO (100) surface illustrating how MARVIN creates an infinite surface with semi-infinite depth. The centre contrasting atoms are the 2-dimensional unit cell. The top “light” region is region 1, and lattice repeats of region 1. The bottom “dark” region is region 2.

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5 Conditions for distribution

Presently, MARVIN is distributed free of charge as an executable only. The source code is available to groups that wish to establish a collaboration with the authors on specific projects requiring code development.

For information about the availability of the code and a rough draft of the manual please contact me at: “dgay@ricx.ri.ac.uk”.

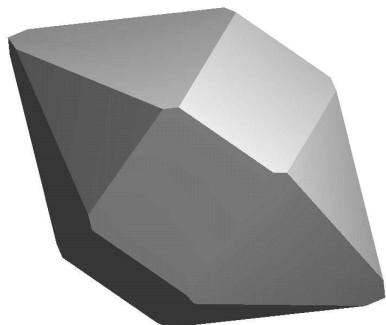


Figure 2: Growth morphology of α -quartz, based on relaxed attachment energies computed by MARVIN. This is very similar to geological samples of quartz.

We have not had any trouble porting the code to any of the following workstations: IBM/RS6000, SGI, HP, Sun Sparc, and DEC.

References

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