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► To cite this version:

Scott Marcus Woodley, Andrew M Walker. New software for finding transition states by probing accessible, or ergodic, regions. *Molecular Simulation*, 2007, 33 (15), pp.1229-1231. 10.1080/08927020701714579 . hal-00515021

HAL Id: hal-00515021

<https://hal.science/hal-00515021>

Submitted on 4 Sep 2010

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Journal:	<i>Molecular Simulation</i> / <i>Journal of Experimental Nanoscience</i>
Manuscript ID:	GMOS-2007-0115.R1
Journal:	Molecular Simulation
Date Submitted by the Author:	28-Sep-2007
Complete List of Authors:	Woodley, Scott; UCL, Chemistry Walker, Andrew; University of Cambridge, Department of Earth Sciences
Keywords:	Ionic diffusion, Ergodic regions, Software, Transition states

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Manuscripts

New software for finding transition states by probing accessible, or ergodic, regions

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Keywords: Ionic diffusion; Ergodic regions, Software; Transition states*Running title:* Finding transition states

An automated, iterative approach to finding the lowest energy, ionic diffusion paths through a periodic structure has been developed within our new code (written in FORTRAN 77 and named *Bubble*). The approach is quite general in that it can be applied to find the accessible (ergodic) regions, at a chosen temperature, of a hyper-surface, which is defined across a uniform grid. We describe both our implementation within the *Bubble* code and its application to locating the approximate transition states for Mg interstitial diffusion in forsterite, which can then be refined using standard transition state searching [1].

In computational studies of diffusion within ionic crystals, it is necessary to be able to identify transition states, which are the least stable atomic configurations through which the system must evolve during an individual hopping event. Transition states, or saddle points, are represented by particular first-order turning points on a (3N-3) dimensional energy hyper-surface, dimensions of which are the atomic coordinates. We initially require the approximate location and configuration of the relevant turning point, defined on a three-dimensional subspace where the diffusing atom is held fixed and the other atoms relaxed so as to minimise the lattice energy. For vacancy diffusion the approximate configuration of the transition state is known (broadly, an interstitial located somewhere between two lattice sites), but for interstitial diffusion the configuration of the transition state can be less obvious. Thus we evaluate a large area of the potential energy surface, as a function of the moving interstitial magnesium ion position. More precisely, the diffusing Mg(II) interstitial was fixed on a uniform grid covering the whole symmetry irreducible portion of the unit cell, whilst the ions in the extended neighbourhood were relaxed. Once this potential energy surface has been mapped, the problem becomes one of finding suitable approximate saddle points: the grid of energy points becomes the input data for our *Bubble* code to search.

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3 A flow chart of the *Bubble* code is shown in figure 1. For ease of explanation consider an
4 analogous problem on a two dimensional topography, discretised over a regular $n \times m$ grid, where
5 height represents the energy. In our example the grid spans the 3×3 supercell of the crystal. The
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7 lowest point, or global minimum (GM), in the central unit cell is located by comparing all data. Next
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9 the code finds the lowest paths to the equivalent points in the adjacent unit cells; the highest point
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11 along such a path being the transition point. Imagine the effect of pouring water onto the GM of the
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13 central unit cell. As the basin containing the GM fills, water may spill out into higher basins.
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15 Eventually, one of the surrounding equivalent lowest basins will flood. The vector from the central
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17 GM to one of the newly wet GM is the direction of diffusion. At this stage, one of the highest wet
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19 points is the transition state from one GM to the other. Adding more water will allow the transition
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21 states in the other directions to be found.
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25 In our simulation, initially all grid points, apart from the lowest point in the central unit cell,
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27 are labelled as dry. Each time the water level is raised, the relative height of dry grid points that are
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29 nearest neighbours to wet grid points are checked; if below the water level then it is labelled as wet.
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31 Even for the smallest rise in water level, it is important to check the nearest neighbouring dry grid
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35 height of the dry and wet grid point is less and higher than the previous water level, respectively,
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37 then the coordinates of the wet grid point are stored as it represents a saddle point. Each time the
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51 investigate the shape/size of higher energy ergodic regions). In the actual case of diffusion in a
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53 crystal, the system is periodic in three directions and we thus simulate an expanding bubble on a
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55 3D grid and the code loops over grid points that define the surface of this bubble (see figure 2).
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3 The speed of the *Bubble* code depends upon both the number of grid points (which in turn
4 depends on the required accuracy and system size) and the step size for the water level. Upon
5 flooding into a basin containing one of the periodic images of the GM, the previous surface of the
6 bubble can be reloaded and a smaller step taken so to reduce the number of candidate points.
7 (Alternatively, although less efficient, as the code requires less than a minute on a typical desktop
8 computer, successive runs of the code with ever decreasing step size could be performed). Once
9 the approximate transition states are located, the second order transition state search can be
10 implemented to allow for refinement of the transition structure with motion of the diffusing ion away
11 from the grid points. In our example, a grid of 20×40×20 points across the unit cell for forsterite (two
12 neighbouring grid points 0.25 Å apart) was sufficient. The *Bubble* code can also employ the
13 appropriate space group symmetry, so reducing the 16000 energy calculations to a more
14 manageable 2000.
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27 From experimental data [2], the mechanism of diffusion in forsterite is uncertain. Using
28 *Bubble*, as well as finding the migration paths for diffusion, it was found that interstitial Mg diffusion
29 has a higher activation barrier than O vacancy diffusion in all three crystallographic directions, (e.g.
30 3.13 compared to 0.72 eV in the [001] direction) so suggesting the mechanism is by vacancy
31 diffusion [3].
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37 [1] A. Banerjee, N. Adams, J. Simons, R. Shepard. Search for stationary points on surfaces. *J.*
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41 [3] A.M. Walker, S.M. Woodley, B. Slater, K. Wright. A computational study of magnesium point
42 defects and diffusion in forsterite. Submitted.
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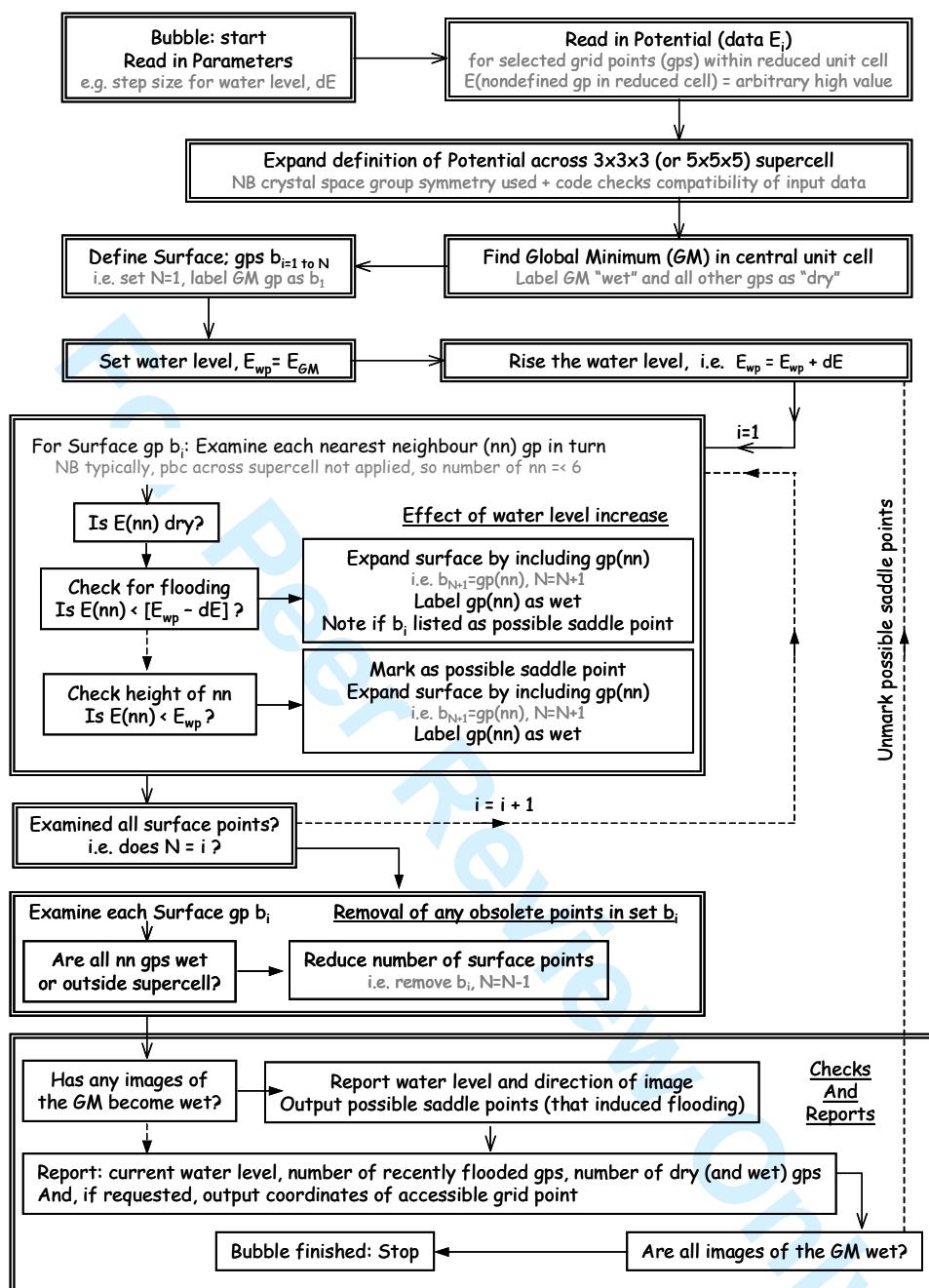
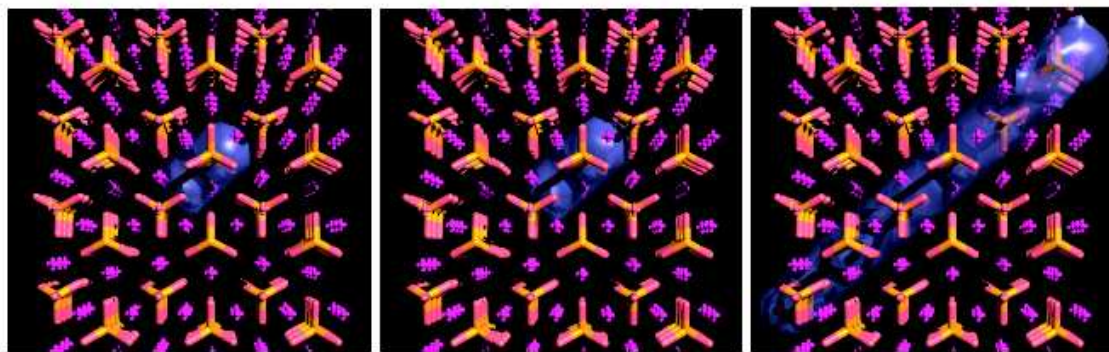


Figure 1: Flow chart of the Bubble code: solid arrowheads of solid (broken) lines indicate direction of yes (no).



(a) The global minimum

(b) Just prior to reaching a transition state

(c) After reaching the transition state

Figure 2: The growing bubble marks the accessible volume for hydrogen diffusion in forsterite crystal structure at a temperature (a) near 0K, (b) just below and (c) above the transition temperature.

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In computational studies of diffusion within ionic crystals, it is necessary to be able to identify transition states, which are the least stable atomic configurations through which the system must evolve during an individual hopping event. Transition states, or saddle points, are represented by particular first-order turning points on a $(3N-3)$ dimensional energy hyper-surface, dimensions of which are the atomic coordinates. We initially require the approximate location and configuration of the relevant turning point, defined on a three-dimensional subspace where the diffusing atom is held fixed and the other atoms relaxed so as to minimise the lattice energy. For vacancy diffusion the approximate configuration of the transition state is known (broadly, an interstitial located somewhere between two lattice sites), but for interstitial diffusion the configuration of the transition state can be less obvious. Thus we evaluate a large area of the potential energy surface, as a function of the moving interstitial magnesium ion position. More precisely, the diffusing Mg(II) interstitial was fixed on a uniform grid covering the whole symmetry irreducible portion of the unit cell, whilst the ions in the extended neighbourhood were relaxed. Once this potential energy surface has been mapped, the problem becomes one of finding suitable approximate saddle points: the grid of energy points becomes the input data for our *Bubble* code to search.

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[1] For a random-walk approach on a hypersurface, see, for example, J.C. Schön, H. Putz, M. Jansen. *Studying the energy hypersurface of continuous systems - The threshold algorithm*. *J. Phys.-Conden. Matt.*, **8**, 143 (1996).

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[2] A. Banerjee, N. Adams, J. Simons, R. Shepard. Search for stationary points on surfaces. *J. Phys. Chem.*, **89**, 52 (1985).

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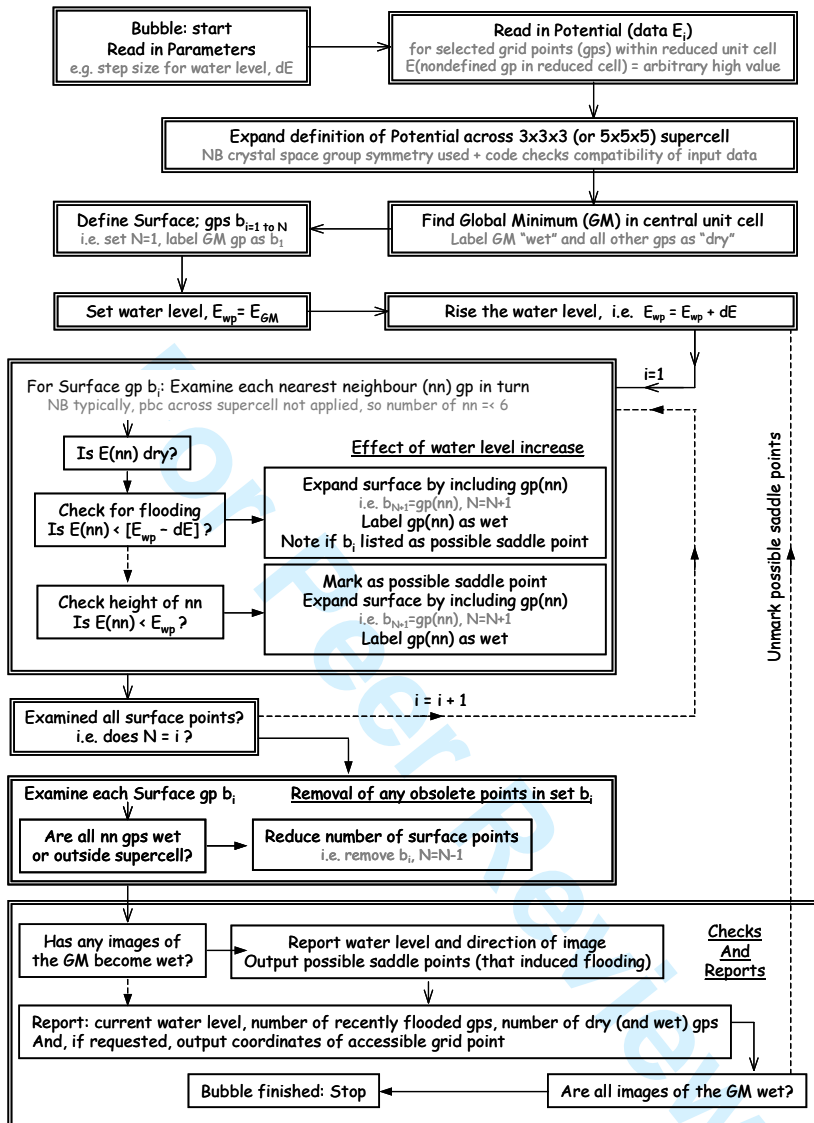


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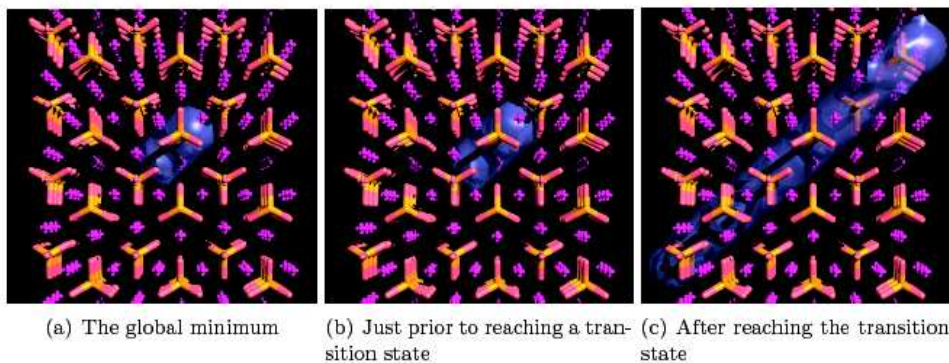


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