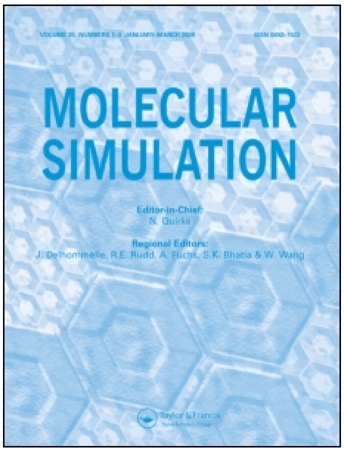

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

An efficient technique for the prediction of solvent-dependent morphology: the COSMIC method

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To cite this Article Gale, J. D. and Rohl, A. L.(2007) 'An efficient technique for the prediction of solvent-dependent morphology: the COSMIC method', Molecular Simulation, 33: 15, 1237 — 1246

To link to this Article: DOI: 10.1080/08927020701713902

URL: http://dx.doi.org/10.1080/08927020701713902

Molecular Simulation, Vol. 33, No. 15, December 2007, 1237–1246

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An efficient technique for the prediction of solvent-dependent morphology: the COSMIC method

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(Received September 2007; in final form September 2007)

We have developed a method of calculating the solvation energy of a surface based on an implicit solvent model. This new model called COSMIC, is an extension of the established COSMO solvation approach and allows the technique to be applied to systems of any periodicity from finite molecules, through polymers and surfaces, to cavities of water within a bulk unit cell. As well as extending the scope of the COSMO technique, it also improves the numerical stability through removal of a number of discontinuities in the potential energy surface. The COSMIC model has been applied to barium sulfate, where it was found to produce similar surface energies and configurations to the much more computationally expensive explicit molecular dynamics simulations. The calculated solvated morphology of barium sulfate was found to differ significantly to that calculated in vacuum with a reduced number of faces present.

Keywords: Solvation; Surface energy; Barium sulfate; COSMO

1. Introduction

One of the most readily appreciated properties of a crystalline material is its shape, since it is often a macroscopic observable. However, the morphology of a substance can often vary quite considerably, according to whether the crystal was grown by vapor deposition or by crystallization from a solvent, not to mention the presence of impurities or growth modifiers.

There is a long history of attempts to be able to predict and understand the morphologies that crystals exhibit. One of the simplest approaches is the Bravais–Friedel–Donnay–Harker (BFDH) method [10] that determines the likelihood of appearance of a specific crystal face in the morphology based upon the interplanar spacing. This approach only depends on the unit cell dimensions and space group symmetry, rather than the particular atomic structure within the crystal. More realistic is to determine the morphology with specific reference to the crystal structure via some thermodynamic assessment of the possible surfaces. Two criteria are widely used, particular in atomistic force field simulation, though they are equally applicable to quantum mechanical descriptions—namely the surface energy and attachment energy [14]. The surface energy is the energy required to cleave a particular crystal face, starting from the bulk material and is usually expressed per unit area. Based solely on the thermodynamic criterion that the crystal shape will be such that the total surface energy (strictly free energy) will be minimized, it is then possible to determine the likely morphology through using a Wulff construction [29]. Here, the low energy faces will then be those that dominate the morphology. Alternatively, it is possible to use the attachment energy as a criterion. This is the energy released through the addition of a growth slice to the surface. Although, formally also a thermodynamic quantity the argument is often made that the faces with the most exothermic attachment energy will grow fastest and therefore be least expressed in the morphology.

Both the surface and attachment energies have been extensively used to predict the morphologies of many types of material from organic molecular crystals through to dense inorganic solids. Despite the many successes of the approach, the assumption has nearly always been made that the material is grown from vacuum, which is clearly not the case for many substances. The question is how to include the presence of solvent in morphology calculations in an effective manner. One possibility

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Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020701713902

is to explicitly solvate each surface with the appropriate solvent and then to perform molecular dynamics to sample the ensemble of possible solvated configurations. While this approach can be done, and indeed yields detailed and valuable information, it is also very expensive. Given that many different crystal faces have to be considered for a single morphology, the determination of surface energies in the presence of solvent using this brute-force approach is far from ideal. Some workers have tried to simplify the process by considering the binding of a small number of molecules of water to several surfaces as a measure of solvent stabilization [8]. However, this is clearly someway from full hydration.

An important point to note with regard to surface energies is that the absolute magnitudes do not matter in the determination of morphology—only the ratio. This is one of the reasons for the success of morphology calculations based on atomistic methods. Hence, to perform extensive molecular dynamics studies in order to predict a crystal shape in the presence of solvent should be unnecessary and inefficient in all but the most subtle cases. Here, we propose an alternative, more efficient, approach based on continuum solvation models, such that the details of the solvation are sacrificed for a fast calculation of the solvation energy. The proposed COSMIC scheme to be described in the present work is a modification of the established COSMO method [17] for molecular solvation, adapted for the application to surface calculations.

2. Methodology

The aim of the present work is to determine the surface energy of a crystal face in the presence of a continuum description of a solvent. For simplicity, we will describe the technique used in terms of an atomistic simulation approach with a force field description of inter-atomic interactions. However, the method described is general and could equally as well be applied to quantum mechanical calculations.

In order to calculate the surface energy of a material, we consider the widely used two region approach within 2D boundary conditions. Here, an infinite slab of the crystal cleaved to expose the face of interest is divided into region one, in which the atoms are allowed to fully relax to equilibrium and region two, in which the atoms are frozen at the bulk optimized coordinates. Similarly, the 2D lattice parameters are fixed at the equilibrium bulk values. Here, the purpose of region two is to provide an accurate description of the bulk potential acting on the atoms in region one. Consequently, it is necessary to increase the number of layers within the two regions until the surface energy reaches convergence. Usually, the upper surface is in contact with vacuum. However, here we consider it to be solvated instead.

There is an extensive literature on the computational approaches to solvation of both molecules and ions which has been reviewed elsewhere. Such techniques can be broadly divided into methods that involve either a cavity or a solvent accessible surface about the species, at which the influence of the molecular potential on the solution is determined, or alternatively the Poisson/Poisson–Boltzmann equation [15] is solved on an extended mesh of points through out the solvent. Within these classes there are many further variations.

Here, we have decided to base the determination of the solvation energy on the conductor-like screening model (COSMO) of Klamt and Schuurmann [17], which has been extensively implemented in many semi-empirical and *ab initio* quantum mechanical codes. The basis of the method is that the solvent is assumed to behave as a perfect conductor situated around a solvent accessible surface that will be defined later. The charges induced on the surface due to the electrostatic potential of the enclosed species are then determined and subsequently scaled to those appropriate to the dielectric constant of the solvent ϵ, by multiplying by a factor f, that is given by:

$$f = \frac{(\epsilon - 1)}{(\epsilon + (1/2))}$$

There is also a variant of the original scheme, referred to as GCOSMO [27], in which the factor of a half is dropped from the denominator given above, as well as other modifications to the approach.

To date, the COSMO method has been predominantly applied to the solvation of finite species. Although, the GCOSMO method has been applied to the liquid–solid interface [26], this was performed using an embedded cluster approach and so remained formally an aperiodic method. The challenge here is to adapt the COSMO scheme for periodic systems. During the course of developing the present method, two other implementations of periodic COSMO have appeared (we note that preliminary applications of our method have appeared in earlier works [6,22]). Firstly, Cossi [7] described an algorithm for computing the electrostatic potential for the COSMO method within 1 and 2D boundary conditions based on the sum of Legendre polynomials. Secondly, Delley [9] recently described the adaption of the COSMO method within the DMol3 program to 3D boundary conditions. In the present work, we describe our fully general implementation of the periodic COSMO model for 1–3D periodicity, including analytical derivatives to second order which has been implemented within the force field code GULP [13]. As well as adapting the scheme for periodic boundary conditions, it was also found beneficial to make several other modifications to the original COSMO algorithm. Thus, we will describe the method below in detail.

2.1 Construction of the solvent accessible surface

Before considering how the induced charges and energy are determined, the first requirement is to determine the solvent accessible surface. Here, as in most models the surface is represented by a grid of points that lie on the surface. Each atom is assigned a radius, r_A, which is an empirical parameter, as is the solvent molecule, r_S. Points are then created on the surface of a sphere of combined radius $r_A + r_S$ about each atom. Any points that lie within the volume of an adjacent atom are excluded from the surface. Clearly, it is possible to create a more realistic solvent accessible surface by considering the solvent particle rolling around the surface of the species. This would remove the discontinuity in the curvature of the surface where two or more atoms begin to overlap. However, the advantage of the above COSMO scheme is that each point remains strictly a function of the coordinates of a single atom, which makes evaluation of forces straightforward. A more realistic, smooth, surface requires more complex curvature matching conditions to create the surface and the forces become intrinsically many-body.

Under the COSMO algorithm, once the above surface has been created, then the radius associated with each point is reduced by a constant amount, δ_s, which is a solvent specific parameter. The effect of this is to remove the sharp cusps in the solvent accessible surface and as will be seen later, removes the potential for a discontinuity in the electrostatic interaction between induced charges on the surface.

The use of the above contraction of the solvent radius also has a further benefit. For relative open molecular crystalline structures the optimal solvent accessible surface distance from the solvated atoms, in terms of the energetics, often leads to the creation of solvent bubbles within the bulk structure, which is incorrect. By constructing the solvent accessible surface based on a larger radius and then displacing it inwards the formation of such solvent pockets can be avoided.

The above describes the essence of the COSMO algorithm for the construction of the solvent accessible surface. However, our algorithm for the creation of the surface deviates through the imposition of two additional requirements that were not satisfied by the original approach:

1. The solvent accessible surface must be smooth and continuous.
2. The solvent accessible surface must be rotationally invariant for molecules and maximize the preservation of symmetry.

The first of the above requirements is needed to ensure the successful optimization of structures, since discontinuities create false local minima, as well as to ensure that derivatives obtained analytically are consistent with those determined by finite differences. The second criterion is introduced to ensure that the same answer is obtained regardless of the choice of absolute Cartesian orientation specified and to remove numerical symmetry breaking effects.

The nature of the discontinuity in the solvent accessible surface is obvious because the number of points on the surface of each atom is finite and as the atoms move points can change from being excluded, because they lie within the volume of another atom, to being included. This can be remedied by the introduction of a switching function that smoothly changes from 0 to 1. Hence, we introduce a weighting factor for the point i of w_i. Here the weight is given by:

$$w_i = \prod s(r_{ij})$$

where $s(r_{ij})$ could potentially be any smooth unit switching function. Formally, the product runs over all atoms and their periodic images. However, only atoms where the switching function is not unity need be considered. Here we use a fourth order polynomial taper function, with the boundary conditions being the function values and that the derivatives should be zero. The same approach of introducing a product of smoothing functions has been taken by Senn *et al.* [24] in their modification of the COSMO scheme for use in *ab initio* molecular dynamics, while a similar approach has been taken by Delley during his periodic COSMO implementation [9]. York and Karplus [30] have also demonstrated how the solvent accessible surface can be smoothed through the introduction of Gaussian charge distributions, instead of point charges, at the segments.

The weighting factor described here can then be applied to the induced charges and thus scales the interactions between particles appropriately, as will be discussed later. Although, this indeed leads to a smooth surface, free from discontinuities, there is a price to pay since the analytical derivatives now become more complex.

Satisfying the second criterion for the solvent accessible surface requires a discussion of how the points on each atomic sphere are chosen. Starting from a simple polyhedral shape, in the case of COSMO this being a dodecahedron, additional points are created by sub-triangulation. Given an initial triangular face of a polyhedron, smaller triangles can be created by adding a point either to the center of the current triangle, or by adding points at the mid-point of each edge. Using this approach, the number of points on the surface of a single atomic sphere, N_P, is given by:

$$N_P = 10 \times 3^k \times 4^l + 2$$

where k and l are integers.

If we consider the shape of a dodecahedron, it is actually quite a low symmetry polyhedron, relative to a Cartesian axis set (i.e. if rotated by 90 degrees the distribution of points changes). Hence, it naturally tends to lead to small symmetry breaking forces except at very high levels of triangulation. Consequently, we propose, as have others [30], to use an octahedron as the initial polyhedron from which to derive the mesh of points, since it has a higher symmetry with respect to permuting the Cartesian axes. This is analogous to the preferred choice of the octahedral orders of Lebedev angular quadrature in the numerical integration schemes for spherical harmonics [3]. For an octahedron, the number of points on the surface is now determined according to the following expression:

$$N_P = 4 \times 3^k \times 4^l + 2$$

This change tends to reduce the numerical errors associated with the finite size of the mesh of points. However, it does not lead to rotational invariance of the results for molecules directly. Hence, we apply one further step. Firstly, the non-mass weighted moment of inertia tensor, M, is generated according to:

$$M_{\alpha\beta} = \sum \left(\alpha_i \frac{\sum \alpha_j}{N_a} \right) \left(\beta_i \frac{\sum \beta_j}{N_a} \right)$$

where α and β are Cartesian coordinates, x, y or z, and N_a is the number of atoms in the system. Diagonalisation of this matrix yields a set of eigenvectors that can then be used to transform the orientation of the points for each atom into a standard system that enforces rotational invariance for the final calculation of the solvation energy.

2.2 Determination of the induced charges

The COSMO model is essentially a Coulombic model with induced charges on the grid points of the solvent accessible surface. Hence, if we represent the interactions in matrix form, where A_{ij} represents the Coulomb term between points i and j on the solvent accessible surface, and B_{im} is that between the point i and the charge of atom m, then the energy of the system can be expressed as:

$$U = qBQ + \frac{1}{2} qAq$$

where q is the vector of induced charges on the solvent accessible surface, and Q is the vector of atom-centered point charges. If the induced charges are those that minimize the total energy, then this leads to the following condition:

$$\frac{\partial U}{\partial q} = BQ + Aq = 0$$

Straightforward rearrangement leads to the final expression for the induced charges:

$$q = -A^{-1} BQ$$

The final energy can then be written as:

$$U = -\frac{1}{2} q.V$$

where V is the vector of potential at the solvent accessible surface due to the atomic charges, and is equal to BQ.

It now remains to define the elements of the matrices A and B. Let us first consider the case of an individual molecule from which the natural extension to periodic systems will arise. The elements of the matrix B are simply given by:

$$B_{im} = \frac{w_i}{r_{im}}$$

for the present situation in which every point on the surface has a weight. The elements of the matrix A consist of the Coulomb interaction between points, but also includes the self-energy of a given point, A_{self}:

$$A_{ij} = A_{\text{self}} \partial_{ij} + \frac{w_i w_j}{r_{ij}}$$

$$A_{\text{self}} = 1.05 \times \sqrt{N_P}$$

It is important to consider the asymptotic behavior of the weighting factors as they tend to zero in the above expressions. Since the potential acting on any given point on the solvent accessible surface is linearly dependent on its own weight, the induced charge will also smoothly tend to zero, provided the inverse of the matrix A remains determinate. For this reason, the weighting functions are not applied to the self term in A to ensure that only the off-diagonal terms tend to zero and thus the inverse becomes separable into the product of the results for the points with finite weight and a series of single numbers for the points of zero weight that are not required.

In the original COSMO model, the electrostatics of interaction between points on the solvent accessible surface was evaluated using a hierarchical approach involving segments and points. Here, clusters of points were linked together to form a segment and the above matrices described the interaction between segments, rather than points. At short distances, the electrostatic interaction was evaluated as the sum over the interaction between individual points, whereas at long range the Coulomb term was determined based on the segment position alone. This reduces the dimensions of the matrices and speeds up the evaluation of the Coulomb interactions for large systems. Although, in the present work we will just focus on the direct use of the points for simplicity, we have also retained the option to employ segments too. To ensure smoothness, we have also applied a weighting factor to the inclusion of points in segments, as well as a taper function for the cross over between segment–segment and point–point electrostatics.

To adapt the COSMO method from molecular systems to the periodic case just requires a change in how the Coulomb potential is evaluated. Because of the conditional convergence of the electrostatic sums for both 2D and 3D periodic systems, the potential for the B matrix between the SAS and atomic charges is evaluated using the Parry [19,20] and Ewald techniques [11], respectively. For the case of a 2D periodic surface the expression for the interaction potential between two sites then becomes:

$$\begin{aligned} B_{im} = \frac{erfc(\eta^{1/2} r_{im})}{r_{im}} \quad &+ \frac{\pi}{A}\sum \frac{\exp(iG.r_{im})}{|G|} \\ &\times \left[\exp(|G|z_{im}) erfc\left(\frac{|G|}{2\eta^{1/2}} + \eta^{1/2} z_{im}\right)\right. \\ &\left. + \exp(-|G|z_{im}) erfc\left(\frac{|G|}{2\eta^{1/2}} - \eta^{1/2} z_{im}\right)\right] \\ &- \frac{2\pi}{A}\left[z_{im} erf(\eta^{1/2} z_{im}) + \frac{\exp(\eta^{1/2} z_{im}^2)}{(\pi\eta)^{1/2}}\right] \end{aligned}$$

For 1D periodic systems the Coulomb sum is now absolutely convergent. However, the rate of convergence is slow and therefore we employ the technique of Saunders *et al.* [23] to accelerate the summation.

While it might appear that the same expression for the Coulomb matrix elements could be used for the A matrix, as described for the B matrix above, this turns out not to be the case in general. The sum of the Coulomb interactions due to the Parry sum is given to within a constant by the above expression. When summing over a charge neutral system this offset is cancelled and a well-defined value is obtained, as is the case for B where the underlying surface is uncharged. However, in the case of the interactions between points on the solvent accessible surface, the imposition of charge neutrality is not explicit in the elements of the A matrix and therefore for periodic systems the values are only defined to within a constant offset. Unfortunately, the final solvation energy is not invariant with respect to the value of the offset and consequently a different approach must be taken.

To resolve the aforementioned difficulty we have chosen to use the real-space summation technique of Wolf *et al.* [28] to evaluate the elements of the A matrix, since this avoids the problem and leads to a well defined set of matrix elements, regardless of dimensionality. The resulting expression for the elements of A is:

$$A_{ij} = A_{\text{self}}\partial_{ij} + w_i w_j\left(\frac{erfc(\alpha r_{ij})}{r_{ij}} - \frac{erfc(\alpha r_{\text{cut}})}{r_{\text{cut}}}\right)$$

where α is a convergence parameter, similar to $\eta^{1/2}$ in the Ewald/Parry summation, that controls the rate of decay in real space, and r_{cut} is the cutoff radius at which the potential is forced to go to zero. Although, the use of the Wolf sum will typically lead to a small deviation from the pure Coulomb result, unless very tight and expensive convergence is requested, the discrepancy can be factored into the parameterization of the COSMO model. In the present work, we choose values of $\alpha = 0.01\,\text{Å}$ and $r_{\text{cut}} = 110\,\text{Å}$, in order to achieve tight convergence to the Coulomb limit, but more rapid decay can be achieved for different values of α in order to trade efficiency for precision.

2.3 The COSMIC algorithm

In the foregoing section, the description of how to adapt the COSMO method to periodic systems is described. However, there is a further complication, which necessitates a change in the algorithm. When working with periodic systems, it is a necessary requirement for convergence of the electrostatic sums that the unit cell be charge neutral. While this is obeyed, by construction, for the sum of atomic charges within the system, the COSMO method places no constraint on the total induced charge on the solvent accessible surface. Consequently, the COSMO algorithm naturally leads to charge systems in almost every case.

One possible solution to the charge neutrality problem in 3D periodic systems is to add a neutralising background charge, as has been widely applied in supercell studies of defects. However, there is no straight forward extension of this approach to lower periodicities and therefore this solution is not suited to the study of surface problems.

Here we propose a modified algorithm, which we refer to as the COnductor-like Screening Model with Integer Charge (COSMIC). Under this scheme, the COSMIC induced charges, q^C, are given by:

$$q^C = q - w\left(\frac{(\sum q_i)}{(\sum w_i)}\right)$$

where w is the vector of weights for the points on the solvent accessible surface. The justification for the above definition is that it guarantees that the solvent accessible surface will be charge-neutral by design, and therefore the total system will also be neutral. Furthermore, weight factors are included, as appropriate, to ensure that the variation of the induced charges is smooth with respect to changes in the number of points on the surface.

2.4 The COSMIC energy and analytic derivatives

Given the above constraint on the induced charges on the solvent accessible surface, the expression for the COSMIC energy becomes:

$$U_{\text{COSMIC}} = q^C BQ + \frac{1}{2} q^C A q^C$$

Turning now to consider the first derivatives of the energy with respect to the structural variable, as required for geometry optimization, the expression is obtained by piecewise differentiation of the terms:

$$\begin{aligned} \left(\frac{\partial U_{\text{COSMIC}}}{\partial \beta}\right) = (BQ + q^C A)\left(\frac{\partial q^C}{\partial \beta}\right) + q^C\left(\frac{\partial B}{\partial \beta}\right)Q \\ + \frac{1}{2} q^C\left(\frac{\partial A}{\partial \beta}\right) q^C \end{aligned}$$

The derivatives of the induced charges on the solvent accessible surface are in turn given by:

$$\left(\frac{\partial q}{\partial \beta}\right) = -A^{-1}\left(\frac{\partial A}{\partial \beta}\right)q$$

from which the differential of the constrained charges can be readily obtained. Higher order derivatives can similarly be readily computed. The above expressions for the energy and analytic derivatives up to second order have been implemented in a development version of the program GULP [13].

3. Results

As an illustration of the application of the COSMIC approach we have chosen to examine the morphology of the mineral barite. This is a relatively insoluble material that occurs as a common scale in many industrial and oil drilling processes [4,25]. Aside from the interest in the crystal growth of this material, it represents a suitable test case since there have been two previous studies in which the solvated surface energies have been determined for the three dominant crystal faces via explicit molecular dynamics. In the present work, we utilize the COSMIC algorithm to examine the change in morphology induced by hydrating the surfaces of $BaSO_4$ in order to contrast this with the results of explicit solvation [16,21].

As a force field, we initially took the parameters reported by Piana *et al.* [21] in their molecular dynamics study of the structure of barium sulfate surfaces in the presence of explicit water molecules. Having optimized the bulk structure of barium sulfate, the 11 most favorable symmetry unique surfaces, as ranked according to the BFDH methodology, were chosen for study. Using the program GDIS [12], the allowed non-dipolar surface cleavage planes were determined and the sizes of regions one and two were converged with respect to the surface energy based on unrelaxed calculations. Subsequently, the structure of region one was relaxed to convergence for each surface *in vacuo*. The unrelaxed and relaxed surface energies are given in table 1.

In figure 1, we illustrate the unrelaxed and relaxed crystal habits *in vacuo* based on the surface energies, to yield the equilibrium morphologies. The Piana *et al.* potential set predicts an unrelaxed morphology consisting of {001}, {210}, {211} and {010} facets. Relaxing the surfaces has the effect of removing the {010} facets whilst greatly reducing the {211} facets.

Before undertaking surface simulations including implicit solvation, it is necessary to fix the parameters that go into the COSMIC model, namely the atomic radii, as well as the radius and polarization center offset of water. In addition, there are the parameters that control the numerical aspects of the calculation, as well as the non-empirical parameters, such as the dielectric constant of water, which we take to be 78.4. Given the large number of possible parameters, as against the number of observables,

Table 1. Unrelaxed and relaxed surface energies for the low index faces of barium sulfate under *in vacuo* conditions.

Surface (hkl)	*Shift*	*Unrelaxed surface energy (Jm^{-2})*	*Relaxed surface energy (Jm^{-2})*	*% change*
(101)	0.00	1.124	0.843	−25
	0.30	1.711	1.101	−36
	0.50	1.294	0.932	−28
	0.70	1.711	1.305	−24
(100)	0.00	1.354	0.922	−32
	0.25	1.322	0.951	−28
(011)	0.00	1.663	1.102	−34
	0.50	1.706	1.220	−29
(111)	0.00	1.760	1.081	−39
	0.16	1.588	1.174	−26
	0.50	1.217	0.873	−28
	0.84	1.588	1.000	−37
(201)	0.00	1.376	0.941	−32
	0.50	1.512	1.122	−26
(001)	0.00	0.610	0.553	−9
	0.25	1.665	1.258	−24
(210)	0.00	1.121	0.823	−27
	0.50	0.677	0.502	−26
(102)	0.00	1.773	0.944	−47
	0.10	1.717	1.230	−28
	0.50	1.641	1.107	−33
	0.90	1.717	1.090	−36
(211)	0.00	1.023	0.801	−22
	0.10	1.758	1.169	−34
	0.50	0.811	0.691	−15
	0.90	1.758	0.908	−48
(112)	0.00	1.413	0.937	−34
	0.15	1.694	1.058	−38
	0.50	1.586	1.055	−33
	0.85	1.694	1.100	−35
(010)	0.00	0.961	0.820	−15

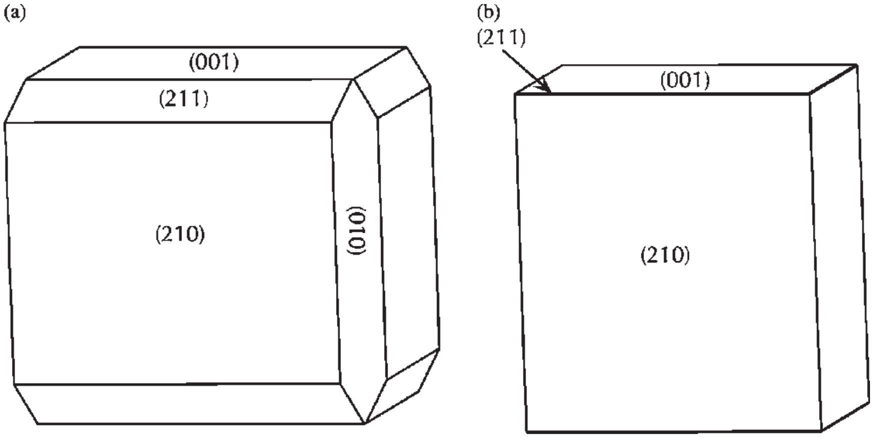

Figure 1. *in vacuo* (a) unrelaxed and (b) relaxed equilibrium morphology of barium sulfate.

we have chosen to make some simplifying assumptions. Firstly, the radius of water has been set to 1.4 Å and the radius shift of water was then set equal to the radius, as is widely done. Secondly, the radii of the atoms Ba, S and O were set to 2.18, 1.50 and 1.48 Å respectively, which reproduce the solvation energies of the barium and sulfate ions [18].

The remaining numerical parameters were set to achieve a reasonable balance between precision and computational efficiency. The number of points and segments per atom was set equal to 326. A smoothing range of 0.2 Å was used to ensure continuous behavior of the energy surface.

All of the surfaces considered *in vacuo* were relaxed in the presence of the implicit aqueous solvent and the resulting surface energies are given in Table 1. Note that all the values are lower than the equivalent surface energies *in vacuo* due to stabilization of the interface by the solvent. In fact, the reduction is quite uniform with the unrelaxed surface energies decreasing by an average of 46.2% with a standard deviation of 5.0%. The relaxed surface energies show very similar behavior with an average decrease of 46.4% and a standard deviation of 8.1%.

These calculated solvated surface energies can be compared to those calculated using the explicit inclusion of water molecules via molecular dynamics simulations in the work of Piana *et al.* The MD averaged surface energies calculated by Piana and coworkers for the (001), (010) and (210) surfaces are 0.241(18), 0.193(15) and 0.194(15) Jm^{-2}, respectively. The values using an implicit water solvation model are 0.276, 0.479 and 0.241 Jm^{-2}, respectively, as shown in Table 1. The (001) and (210), faces have solvated energies slightly higher than the molecular dynamics results with both methodologies yielding the (001) higher in energy than the (210). The implicit solvation energies, however, were calculated in a fraction of the time (under 190 s for (001) and under 15 min for (210) on a single 1.5 GHz Itanium 2 processor of an SGI Altix 3700 BX2 system) that would be required for the MD results (typically days). Clearly, there is significant disagreement for the solvated surface energy of the (010) surface. Piana *et al.* [21] have already demonstrated that this surface is in some sense anomalous in that it exhibits fast nucleation, with the sulfate ion assisting barium ion desolvation. A failing of implicit solvent modeling is that it fails to describe the situation where strong localized hydrogen bonding occurs at specific sites. Hence, it is likely that this is the case for the (010), and may be responsible for the discrepancy. In future work this may be overcome through inclusion of an explicit monolayer of water, supplemented by the COSMIC solvation model.

Some indication of how solvation affects the surface relaxation can be gained by examining how the z-coordinate of the uppermost Ba and S atoms change as the surface relaxes both *in vacuo* and with the solvent present. On the (001) surface, the Ba atom relaxes 0.06 Å into the surface *in vacuo* and only 0.02 Å in water, whereas the S atom relaxes out of the surface by 0.07 Å in vacuum but into the surface by 0.03 Å in water. On the (210) surface, the outermost Ba is found to relax out of the surface by 0.13 Å *in vacuo* and extends to 0.18 Å in water, whilst the outermost S atom relaxes out of the surface by 0.14 Å *in vacuo* but only by 0.11 Å in water. These results suggest that the solvent acts to mitigate the surface relaxation observed in vacuum. These results for the Ba atoms are consistent with the MD results of Piana *et al.*, where they state that the Ba atoms on these two surfaces are found to have displacements less than 0.2 Å. They also observed that the surface sulfates are found to partially rotate and the same is found here, though the rotation on the solvated surfaces is less than that observed on the vacuum surfaces.

The resulting thermodynamic morphologies are shown in figure 2. In both cases, the effect of the solvent is to remove a face from the morphology. In the unrelaxed system the (010) face disappears, whilst in the relaxed system it is the (211) face that disappears.

The Piana *et al.*, potential produces an *in vacuo* relaxed equilibrium morphology with very few facets, so it is difficult to make general observations regarding the effects of solvation on morphology predicted via the COSMIC model. Thus we repeated the calculations here using another well known barium sulfate potential set, the

Table 2. Surface energies for the low index faces of barium sulfate under aqueous conditions, as represented by the COSMIC implicit solvation model.

Surface (hkl)	*Shift*	*Unrelaxed surface energy (Jm^{-2})*	*Relaxed surface energy (Jm^{-2})*	*% change*
(101)	0.00	0.550	0.427	−22
	0.30	0.865	0.532	−38
	0.50	0.735	0.478	−35
	0.70	0.813	0.587	−28
(100)	0.00	0.802	0.590	−26
	0.25	0.808	0.596	−26
(011)	0.00	0.942	0.646	−31
	0.50	1.021	0.758	−26
(111)	0.00	0.971	0.616	−37
	0.16	0.850	0.610	−28
	0.50	0.664	0.459	−31
	0.84	0.949	0.542	−43
(201)	0.00	0.772	0.471	−39
	0.50	0.821	0.598	−27
(001)	0.00	0.309	0.276	−11
	0.25	0.928	0.686	−26
(210)	0.00	0.663	0.449	−32
	0.50	0.361	0.241	−33
(102)	0.00	0.878	0.585	−33
	0.10	0.657	0.521	−21
	0.50	0.703	0.497	−29
	0.90	0.954	0.608	−36
(211)	0.00	0.596	0.430	−28
	0.10	0.876	0.566	−35
	0.50	0.433	0.373	−14
	0.90	0.987	0.640	−35
(112)	0.00	0.765	0.470	−39
	0.15	0.903	0.531	−41
	0.50	0.829	0.544	−34
	0.85	0.914	0.569	−38
(010)	0.00	0.565	0.479	−15

potential II model from the work of Allan *et al.* [1]. This work is of interest as the effects of relaxation *in vacuo* are qualitatively different to those reported here for the Piana *et al.* potential set. Relaxation for both of the Allan *et al.* potential sets have the effect of increasing the size of the minor facets at the expense of the major facets, as well as introducing new facets into the morphology (cf. Figure 1). This difference was unexpected, since although the potentials in Allan *et al.* were derived for static calculations and the Piana *et al.* potentials for dynamical simulations, the differences between the two Allan *et al.* potentials (model I uses splined intermolecular potentials derived from electron–gas data and has atomic polarization, whereas model II uses Buckingham potentials for intermolecular potentials and has no atomic polarization) are larger than the differences between the potential model II of Allan *et al.* and the Piana *et al.* potentials (which use Lennard–Jones potentials for intermolecular potentials and no atomic polarization).

The relaxed equilibrium morphologies calculated *in vacuo* and in water for the Allan *et al.* potential II set are reproduced in figure 3. The figure clearly shows that the relaxed equilibrium morphology expresses many more facets than that calculated for the Piana *et al.* potential. However, the effect of solvation is similar in both cases in that the number of facets is reduced. In the case of the Allan *et al.* potential II, the (010) facet disappears completely whilst the (211) facets are greatly reduced in size, resulting in a rhombic morphology that is very similar to that predicted by the Piana *et al.* potential

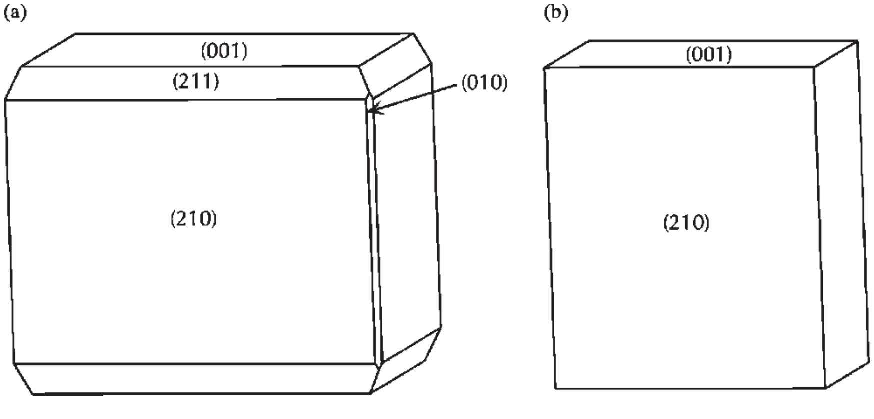

Figure 2. Solvated (a) unrelaxed and (b) relaxed equilibrium morphologies of barium sulfate in water as determined by the COSMIC implicit solvent model for water.

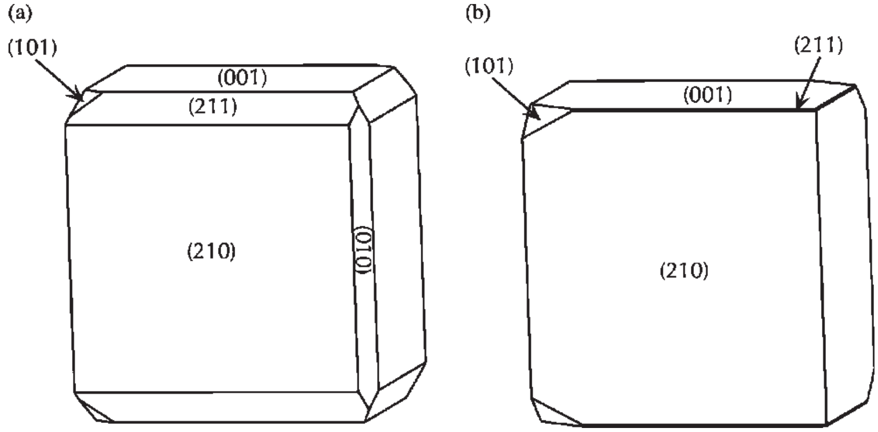

Figure 3. Relaxed equilibrium morphologies of barium sulfate (a) *in vacuo* and (b) in water calculated using the potential II model of Allan *et al.*

in figure 2(b). This rhombic morphology has been observed experimentally by Black and coworkers [5] for crystals prepared from synthetic sea and formation waters. More recently, the thorough work on the morphology of synthetic barite microcrystals by Archibald and coworkers [2] showed that microcrystals prepared in acidified solutions tend to ripen into the stable prismatic form with (001) and (210) faces, strongly suggesting that the solvated morphologies calculated here using the COSMIC model match the observed equilibrium morphologies.

4. Conclusions

In the present work, we described an approach to determining the solvation energy of a surface based on an implicit solvent model. The new model created, known as COSMIC, is an extension of the established COSMO solvation approach that allows the technique to be applied to systems of any periodicity from finite molecules, through polymers and surfaces, through to cavities of water within a bulk unit cell. As well as extending the scope of the COSMO technique, it also improves the numerical stability through removal of a number of discontinuities in the potential energy surface.

The COSMIC model has been applied to barium sulfate, where it was found to produce very similar surface energies and configurations to the much more computationally expensive explicit molecular dynamics simulations. The exception to this is the (010) face where directional hydrogen bonding may be important. Solvation was found to have a significant effect on the calculated morphology of barium sulfate reducing the number of faces present in the morphology.

Acknowledgements

We gratefully acknowledge the initial support of this work through funding from the Australian Research Council under IREX grant no. X00106744. JDG would also like to thank the Government of Western Australia for a Premier's Research Fellowship. Dr Stefano Piana is gratefully acknowledged for valuable discussions. We would like to thank iVEC and APAC for the provision of computing resources.

References

[1] N.L. Allan, A.L. Rohl, D.H. Gay, C.R.A. Catlow, R.J. Davey, W.C. Mackrodt. Calculated bulk and surface properties of sulphates. *J. Chem. Soc. Faraday Discuss.*, **95**, 273 (1993).

[2] D.D. Archibald, B.P. Gaber, J.D. Hopwood, S. Mann, T. Boland. Atomic force microscopy of synthetic barite microcrystals. *J. Crystal Growth*, **172**, 231 (1997).

[3] A.D. Becke. A multicenter numerical integration scheme for polyatomic molecules. *J. Chem. Phys.*, **88**, 2547 (1988).

[4] W.J. Benton, I.R. Collins, I.M. Grimsey, G.M. Parkinson, S.A. Rodger. Nucleation, growth and inhibition of barium sulfate-controlled modification with organic and inorganic additives. *J. Chem. Soc. Faraday Discuss.*, **95**, 281 (1993).

[5] S.N. Black, L.A. Bromley, D. Cottier, R.J. Davey, B. Dobbs, J.E. Rout. Interactions at the organic/inorganic interface: Binding motifs for phosphonates at the surface of barite crystals. *J. Chem. Soc. Faraday Trans.*, **87**(20), 3409 (1992).

[6] M.E. Chu, B. Slater, J.D. Gale. Simulating the dissolution and growth of zeolite beta C. *Angewandte Chemie Int. Ed.*, **44**, 1213 (2005).

[7] M. Cossi. Continuum solvation model for infinite periodic systems. *Chem. Phys. Lett.*, **384**, 179 (2004).

[8] N.H. de Leeuw, S.C. Parker. Surface structure and morphology of calcium carbonate polymorphs calcite, aragonite, and vaterite: an atomistic approach. *J. Phys. Chem. B*, **102**, 2914 (1998).

[9] B. Delley. The conductor-like screening model for polymers and surfaces. *Mol. Simul.*, **32**, 117 (2006).

[10] J.D.H. Donnay, D. Harker. A new law of crystal morphology extending the law of Bravais. *Am. Miner.*, **22**, 446 (1937).

[11] P.P. Ewald. Die berechnung optischer und elektrostatisher gitterpotentiale. *Ann. Phys.*, **64**, 253 (1921).

[12] S.D. Fleming, A.L. Rohl. GDIS: a visualization program for molecular and periodic systems. *Z. Krist.*, **220**, 1 (2005).

[13] J.D. Gale, A.L. Rohl. The general utility lattice program (GULP). *Mol. Simul.*, **29**, 291 (2003).

[14] D.H. Gay, A.L. Rohl. Marvin: a new computer code for studying surfaces and interfaces and its application to calculating the crystal morphologies of corundum and zircon. *J. Chem. Soc. Faraday Trans.*, **91**, 926 (1995).

[15] M.K. Gilson, K. Sharp, B. Honig. Calculating the electrostatic potential of molecules in solution: method and error assessment. *J. Comp. Chem.*, **9**, 327 (1987).

[16] Y.H. Jang, X.Y. Chang, M. Blanco, S. Hwang, Y. Tang, P. Schuler, W.A. Goddard III. The MSXX force field for the barium sulfate–water interface. *J. Phys. Chem. B*, **106**, 9951 (2002).

[17] A. Klamt, G. Schueuermann. COSMO — A new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. *J. Chem. Soc. Perkin Trans. 2*, 799 (1993).

[18] Y. Marcus. Thermodynamics of solvation of ions. Part 5.—Gibbs free energy of hydration at 298.15 k. *J. Chem. Soc. Faraday Trans.*, **87**, 2995 (1991).

[19] D.E. Parry. The electrostatic potential in the surface region of an ionic crystal. *Surf. Sci.*, **49**, 433 (1975).

[20] D.E. Parry. Errata: the electrostatic potential in the surface region of an ionic crystal. *Surf. Sci.*, **54**, 195 (1976).

[21] S. Piana, F. Jones, J.D. Gale. Assisted desolvation as a key kinetic step for crystal growth. *J. Am. Chem. Soc.*, **128**, 13568 (2006).

[22] A.L. Rohl. Computer prediction of crystal morphology. *Curr. Opin. Solid State Mater. Sci.*, **7**, 21 (2003).

[23] V.R. Saunders, C. Freyia-Fa1va, R. Dovesi, C. Roetti. On the electrostatic potential in linear periodic polymers. *Comp. Phys. Commun.*, **84**, 156 (1994).

[24] H.M. Senn, P.M. Margl, R. Schmid, T. Ziegler, P.E. Bloechl. *Ab initio* molecular dynamics with a continuum solvation model. *J. Chem. Phys.*, **118**, 1089 (2003).

[25] K.S. Sorbie, E.J. Mackay. Mixing of injected, connate and aquifer brines in waterflooding and its relevance to oilfield scaling. *J. Pet. Sci. Eng.*, **27**, 85 (2000).

[26] E.V. Stefanovich, T.N. Truong. A theoretical approach for modeling reactivity at solid–liquid interfaces. *J. Chem. Phys.*, **106**, 7700 (1997).

[27] T.N. Truong, E.V. Stefanovich. A new method for incorporating solvent effect into the classical, *ab initio* molecular orbital and density functional theory frameworks for arbitrary shape cavity. *Chem. Phys. Lett.*, **240**, 253 (1995).

[28] D. Wolf, P. Keblinski, S.R. Philpot, J. Eggebrecht. Exact method for the simulation of coulombic systems by spherically truncated, pairwise r^{-1} summation. *J. Chem. Phys.*, **110**, 8254 (1999).

[29] G. Wulff. Zur frage der geschwindigkeitb des wachsthums und der auflosung der krystallflachen. *Z. Kryst.*, **34**, 449 (1901).

[30] D.M. York, M. Karplus. A smooth solvation potential based on the conductor-like screening model. *J. Phys. Chem. A*, **103**, 11060 (1999).