Electrostatic potentials for surfaces of inorganic and molecular crystals

J. D. Foot and E. A. Colbourn*

ICI Chemicals and Polymers Group, Research and Technology Department, The Heath, Runcorn, Cheshire WA7 4QE, UK

The electrostatic potential above surfaces can be useful in ascertaining how molecules will interact with different crystal faces; thus, it can facilitate our understanding of catalytic and crystal growth phenomena. In this paper, we describe a method for calculating the electrostatic potential above surfaces of inorganic and molecular crystals that takes advantage of the regular periodicity of the surface. In addition, we examine the effect of defects at the surface and discuss several applications, including both molecular and inorganic materials.

INTRODUCTION

The concepts of molecular recognition are now widely accepted in theoretical molecular biology and pharmacology. The interaction of a drug molecule with an enzyme, for example, may depend on the geometry and electronic structure both of the enzyme active site and of the interacting molecule, which control the way in which the molecules fit together. The same ideas can be applied in other areas of inorganic and organic chemistry, especially those, like catalysis and crystal growth, in which the interaction of molecules with surfaces is important.

The simplest picture takes into account only the geometry of the interacting species. Thus, we expect that nickel (111) faces, but not the (100) or (110) faces, can facilitate graphite formation, since there is a close match between the lattice spacing of the nickel (111) and graphite surfaces; this templating effect was originally suggested by Leidheiser and Gwathmey.[1] For more complex surfaces, such as those of an inorganic oxide, the symmetry and regularity of the surface can mean that a number of possible adsorption sites exist — above an anion site, above a cation site and between anion and cation sites are only a few of the possibilities. Simple geometrical considerations usually will not suggest an unambiguous binding site for the molecule.

This problem can be overcome partially by calculating the electrostatic potential above a surface; when compared with the electrostatic potential or charge distribution of a molecule, this can provide significant new insight into the orientation and chemisorption of a molecule by a surface. Previous studies in this area have relied on modeling the surface by a small number of molecules or ions, but the Coulomb interaction is long-range, so it may introduce spurious edge effects into the calculation, especially when the surface consists of highly ionic species.

One of the fundamental assumptions underlying our study is that the surface can be represented by an ordered array of point charges, centered at the lattice positions. You can obtain the point charges in a variety of ways; for fully ionic materials, you can use the formal charge, while for molecular crystals, you can obtain partial charges from an analysis of the wavefunction for an isolated molecule. Then you calculate the interaction between a probe proton and the infinite point-ion surface. Since only the Coulomb interaction is evaluated, the process is considerably simpler than that adopted in examining the electrostatic potential of small molecules, where the wavefunction is used explicitly. Hence, this method is of no value in examining interactions on metal surfaces, but in these cases a straightforward geometrical consideration is usually sufficient to indicate likely binding orientations.

The chief problem in calculating the Coulomb interaction of a proton with an infinite surface of point ions is that the Madelung sum is only conditionally convergent. Thus, it is not clear how many molecules must be explicitly included in the surface before it resembles the infinite plane. Harris[2] has suggested several criteria that clusters in the bulk must satisfy in order to model the infinite lattice adequately, including requirements of

zero net charge, zero net dipole and zero net quadrupole. Although you can apply some of these criteria to the case of the surface, it is not sufficient to model the surface simply by splitting the bulk block in half, since this would give an ionicity of species at the surface that is only half that in the bulk — a finding in disagreement with experimental results for at least some systems. Surface rumpling also means that there may be a net dipole for the relaxed surface. There is an additional problem in ensuring that the point ion block so generated is adequate over a range of heights above the surface. Edge effects introduced by assuming a finite block become more important at greater distances.

We have chosen an alternative approach, taking methods developed for calculating long-range Coulomb interactions for infinite planes of ions. These can be adapted to give electrostatic potentials by calculating the interaction of a probe proton with an infinite surface of point ions. By moving the probe proton over a grid of possible sites, a map of the electrostatic potential can be obtained.

THEORETICAL METHODS

Since the Coulomb interaction is long-range, a summation in real space is very slowly convergent. For this reason, Ewald[4] has suggested a procedure that uses both real space and reciprocal space summations, with rapid convergence possible for both parts. This method relies on the three-dimensional (3D) periodicity of the bulk lattice, and although it can be modified for surfaces,[5] we have chosen to adopt a somewhat different approach, suggested by Parry,[6] in which the Coulomb interaction is evaluated in a plane-by-plane summation, again with both real and reciprocal space components. The surface is assumed to be infinite and periodic in two dimensions. Therefore, lattice relaxation and reconstruction are permissible, provided the two-dimensional (2D) periodicity is maintained.

To generate a surface from a unit cell, you need to have the surface lattice vectors for each face that is required. In general, these are not readily accessible; usually the structural information obtainable for crystals involves the lattice spacings a, b and c (not necessarily of the same length or orthogonal to each other) and the angles γ, β and α between them. You can transform these relatively easily to give bulk lattice vectors in Cartesian coordinates, but it is less easy to define the two surface lattice vectors (in Cartesian coordinates) given a Miller index that describes the face. You can do this, however, as follows, provided the Miller indices ($m1$, $m2$, $m3$) and bulk Cartesian lattice vectors $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ are available:

(1) If there is a zero Miller index, the corresponding bulk lattice vector is also a surface lattice vector. If there is a second zero Miller index, both surface lattice vectors will be equivalent to the corresponding bulk lattice vectors. For example, for the (100) surface, the two surface lattice vectors $\mathbf{s}_1$ and $\mathbf{s}_2$ will be equal to $\mathbf{b}_2$ and $\mathbf{b}_3$, respectively.

(2) If there is only one zero Miller index, the surface lattice vector is constructed from the pair of nonzero indices — say, m_1 and m_2 — according to the formula

$$s = -\frac{1}{m_1}\mathbf{b}_1 + \frac{1}{m_2}\mathbf{b}_2$$

If there is no zero Miller index, you calculate each of the two surface lattice vectors from a different pair of nonzero indices according to the same formula.

With these surface lattice vectors, you can generate an infinite surface. Since the unit cell is propagated in only two directions, you need to use a cell unit several layers deep. The Madelung potential is then evaluated using the Parry summation method, with modifications to allow examination of defective surfaces. Although the Parry method can allow for lattice distortion and reconstruction when there is 2D symmetry in the system, treatment of an isolated defect requires additional terms. Suppose R_i are the coordinates of the nondefective system, and r_i describes the equilibrium coordinates (found by solving the force-balance equations) when a defect is introduced. Then the Madelung potential at atom i is

$$\Phi = \Phi_M(r_i) - \sum_j \frac{q_j}{|r_i - R_j|} + \sum_j \frac{q_j}{|r_i - r_j|}$$
$$- \sum_{j \in vac} \frac{q_j}{|r_i - R_j|} + \sum_{j \in int} \frac{q_j}{|r_i - r_j|}$$

where "vac" refers to vacancies and "int" to interstitials. Φ_M is the Madelung potential calculated for the perfect surface from the Parry summation. Note that a substitution can be described as a vacancy plus an interstitial at the same site. You can then calculate the electrostatic potential above the surface by moving a probe proton over a fine grid of sites and calculating the Madelung energy corresponding to its interaction with the surface, assuming that it is a lattice interstitial ion.

We incorporated these concepts into a suite of computer programs. The first program takes the structural information about the crystal (a, b, c, α, β and γ) and, together with the specification of the Miller indices of the surface, gives the surface unit cell and lattice vectors. This program can produce the input file for a second program that calculates the electrostatic potential above the surface. The second program also can take advantage of any symmetry inherent in the system to minimize the computer time required. The NAG library with graphical supplement has been implemented for contour fitting and graphics; different colors distinguish different contours. We have chosen the convention that red contours correspond to the most negative electrostatic potentials and blue ones to positive contour lines. The program runs interactively, requesting information about the size of grid and height above the surface directly from the user and taking information about the lattice structure from previously stored data files. Because the calculation can take several minutes of computer time when there are large unit cells or when there is little symmetry in the system, we have incorporated

a facility for running the actual calculation in a batch mode as well as interactively. It is possible to store both grids and contours and display them subsequently when required.

Testing the program involved two aspects. First of all, we compared the electrostatic potentials above the infinite surfaces with those produced by large, but finite, point ion blocks representing segments of ionic surfaces. Although truncation effects are apparent at the edge of the plot, the contours at the center agree well in both cases. A second check on the calculation is obtained by comparing the potential at large distances with the bulk potential produced by the surface dipole for rumpled surfaces and calculated in a static lattice simulation; these should be equal in magnitude but opposite in signs.

APPLICATIONS

Color Plate 1 shows the electrostatic potential above the (100) surface of MgO. Red contours, corresponding to negative interactions with the proton, lie above anion sites, while blue contours lie above the cation sites. Color Plate 1(a), which corresponds to the perfect unrelaxed MgO surface (treated as a bulk termination), differs slightly from Color Plate 1(b), in which lattice relaxation is assumed. Since there is a slight rumpling of the relaxed surface, with the larger anions lying farther out of the surface (by about 0.05Å) than the cations, a small surface dipole is reflected in the greater attraction that the surface has for cations. Color Plate 2 shows the effect of introducing a defect — in this case a single $[Li^+ - O^-]$ substitutional pair — into the MgO (100) surface.

In Color Plates 1 and 2, an infinite 2D surface is assumed. If a smaller finite cluster is used instead, edge effects become more important. This is illustrated in Color Plate 3, where a finite $7 \times 7 \times 4$ block of point ions, at the perfect lattice positions, is used to represent the MgO (100) surface. Comparison with Color Plate 1(a) shows clearly the effect of omitting the rest of the lattice. With a smaller point ion block, the effects are still more marked.

MgO surfaces are relatively straightforward, since only the cube faces are observed experimentally. For other systems, a number of faces may be of approximately equal energy, and small differences in relative stabilities can dramatically change crystal morphology. An example that has been extensively studied is alpha-alumina,[7] which has a hexagonal structure. In Color Plates 4(a) and (b) we show the electrostatic potentials of (0001) and (10$\bar{1}$0) faces of alumina; it is easy to see that the differences in electrostatic potential for the two surfaces are significant enough to allow the prediction of molecules that would selectively inhibit the growth of one face.

The final application that we will discuss is that of molecular crystals. To determine the point ion charges, we calculated a wavefunction for the molecule and made an analysis of the charge density. We chose as an
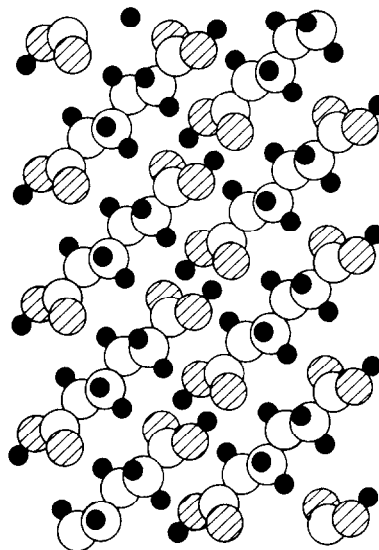

Figure 1. Packing of molecules in adipic acid crystal

example adipic acid and took the partial ionic charges of the isolated molecule from a Mulliken analysis of the MOPAC wavefunction. In spite of the difficulties of using a Mulliken analysis to represent the charge distribution, the method is adequate for the purpose of illustrating our procedures. The packing of adipic acid molecules in a regular crystal is shown in Figure 1. Both the (001) and (100) faces are observed, and the electrostatic potentials of these are shown in Color Plates 5(a) and (b). The most common crystal morphologies appear to be six-sided plates and needle-like crystals, depending on the crystallization medium and rate of precipitation.

The influence of impurities on the precipitation of adipic acid has been discussed by Nielsen,[8] who found that trace amounts of alkanedioic acids and alkanoic acids with less than 12 carbon atoms inhibited the growth of crystals. It has long been established that the presence of trace impurites can affect crystal habit. For example, caproic acid ($CH_3 (CH_2)_4COOH$, which has the same number of carbon atoms as adipic acid) changes both the rate of crystallization and the crystal habit of adipic acid.[9] The electrostatic potential of the (100) face, shown in Color Plate 6, shows that this behavior is expected. We anticipate that the electrostatic potential will be even more useful in designing crystal growth modifiers whose structure differs more substantially from the molecules in the bulk crystal.

CONCLUSIONS

Interactions of molecules with regular crystal surfaces play an important role in studies of areas like catalysis and crystal growth. Simple geometrical considerations can be useful in determining how a molecule fits onto a crystal surface. However, in some cases geometry alone is insufficient to determine the orientation in which the molecule binds and the preferred binding site. In these cases, you can obtain additional information from an

examination of the electrostatic potential above the surface.

The methods of solid-state physics, developed for calculating the Madelung potential at surfaces, can be extended to look at the electrostatic potential above infinite surfaces. This avoids the problem of treating edge effects that are introduced if a finite block is used to represent the surface and that are especially important for ionic solids. It is also possible, in a straightforward fashion, to create either an isolated defect or a regular array of defects in the surface.

ACKNOWLEDGEMENTS

REFERENCES

1 Leidheiser, H., and Gwathmey, A. T. *J. Amer. Chem. Soc.*, 1947, **70**, 1206
2 Harris, F. E. *Theoretical Chemistry: Advances and Perspectives*, Volume 1, H. Eyring and D. Henderson, Eds. Academic Press, New York, 1975
3 Martin, A. J., and Bilz, F. *Phys. Rev. B*, 1979, **19**, 6593
4 Ewald, R. P. *Ann. Physik*, 1921, **64**, 253
5 Mackrodt, W. C., and Stewart, R. F. *J. Phys. C.*, 1977, **10**, 1431
6 Parry, D. E. *Surf. Sci.*, 1975, **49**, 433; *Surf. Sci.*, 1976, **54**, 195
7 Mackrodt, W. C., *et al. J. Cryst. Growth*, 1987, **80**, 441
8 Nielsen, A. E. *Farad. Disc. Chem. Soc.*, 1976, **61**, 153
9 Fairbrother, J. E. Ph.D. Thesis, Department of Pharmacy, University of Nottingham, UK, 1981