Teaching Crystal Structures with 3-D Surfaces

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Abstract: Using mathematics from the method of the exponential scale, crystals inner and outer structures are given. A number of fundamental crystal structures are described as mathematical functions. Plotting the equations gives the classical ball representation of the structures. In the case of intricate structures, the pedagogical interest lies in the possibility of describing the whole structure as the sum of very simple partial structures, each corresponding to a part of the equation. Structures given are primitive cubic packing, primitive hexagonal packing, face-centered-cubic close-packing, hexagonal close-packing, body-centered packing, CsCl, diamond, zinc blende, CaF_2, ReO_3, perovskite, NaCl, Mg_3NF_3, SiO_2, Cu_3Au, NiAs, wurtzite, and graphite.

A crystal-structure dynamics is described. Varying a constant in the equation, it is possible to modify the representation of the structure from small ball-shaped atoms to packing of interconnected polyhedrons and finally to minima-like surfaces. This last description gives a much deeper understanding of the actual structure in term of forces and open spaces. The final, and maybe the main, interest of this concept of surfaces is the possibility of shedding light on the difficult problems of structure–property relationships.

Introduction

In his award address, Arthur B. Ellis, the 1997 winner of the ACS Pimentel award, said, “Among the numerous cutting-edge research areas, many involve the solid state. Yet, until recently, solids were a relatively small part of the chemistry curriculum” [1]. Trying to understand the reasons for that situation, he identifies three obstacles: the specific language, the lack of time in the curriculum, and the difficulty to visualise the structures: “Tools are needed to make these structures comprehensible” [1]. Another reason is the conservatism of textbooks, whatever their level and their quality, as underlined by R. J. Gillespie [2]. Books devoted to this domain are rather scarce. Moreover, the most important textbooks in inorganic chemistry do not consider the structures of solids as significant materials. In a recent French edition of *Inorganic Chemistry*, by Huheey, Keiter and Keiter [3], 38 pages out of 964 are used to describe the packing of atoms, structure maps, defects in crystals, ionic conductivity, band structure, superconductors, and any other topics related to solid structure. Even though the texts might be well-written and beautifully illustrated, almost all of them are restricted to a kind of bestiary of the basic structural types. Yet, over the past fifteen years, new valuable tools have been found that allow a logical description of intricate structures, a better understanding of the correlation between structures and, of utmost importance, the interpretation of their properties. In a search for unifying methods in structural chemistry, a great deal of effort has been devoted to the study of surfaces as mathematical tools to understand the organization of crystalline solids.

Periodic Minimal Surfaces (PMS) were the first surfaces used to furnish useful descriptions of crystal structures. Such surfaces are simply defined as surfaces of zero mean curvature, that is, at each point the sum of both principal curvatures is zero; they correspond to optimal surfaces adopted by soap films. The similarity between PMS and crystal structures was first suggested by A. H. Schoen [4]. The significance of PMS, the equipotential surfaces, and the nodal surfaces, as space partitioners was later developed to describe inorganic or metal structures [5–12].

Recently, a new type of description has emerged. Mathematical functions, calculated with single analytical equations using exponential scale mathematics, give crystal structures directly for the first time ever. This work by S. Andersson and one of us (M. J.) has been reported in a number of papers and in the book *The Mathematics of Structures—the Exponential Scale* [13–17]. A general equation of symmetry has been derived that gives the outer shape (the morphology) of crystals as well as the crystal structure. This involves using functions like the Gauss error function which can be made periodic [15, 18]. In addition, molecules may be described using the method of finite periodicity. An example of this is the description of DNA [19].

In the present paper, we would like to show how the so-called exponential scale can be used for teaching structural chemistry using simple mathematics. This scale can be used at different levels. At the simplest level, the plotting of the equations gives a classical “ball” representation of the structures. In the case of intricate structures, the educational interest lies in the possibility of describing the whole structure as the sum of very simple partial structures, each corresponding to a part of the equation. By varying a constant in the equation, it is also possible to modify the representation of the structure from small ball-shaped atoms to packing of interconnected polyhedrons and finally to minimal-like surfaces. This last description gives a much deeper understanding of the actual structure in term of forces and open spaces. The final, and maybe the main, interest of this concept of surfaces is the possibility that it sheds light on the difficult problems of structure–property relationships.

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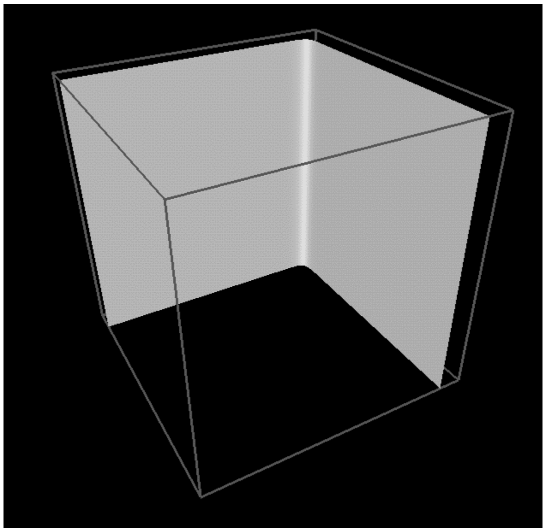

Figure 1. Two planes added on the exponential scale. C = 10^{10}. The function is drawn in the region $-12 < x,y,z < 12$.

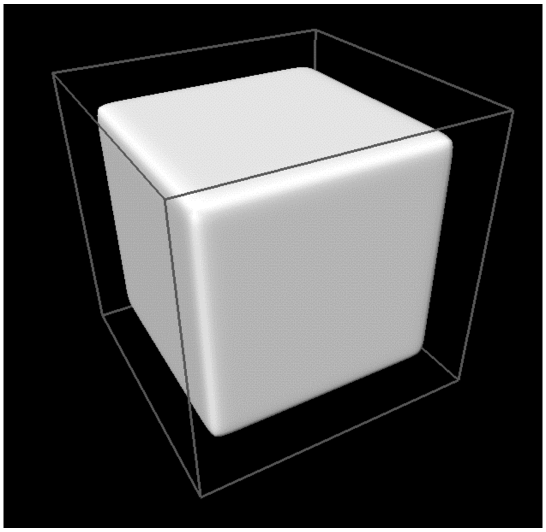

Figure 2. Six planes added on the exponential scale forming a cube with C = 10^{10} and the same boundaries as in Figure 1.

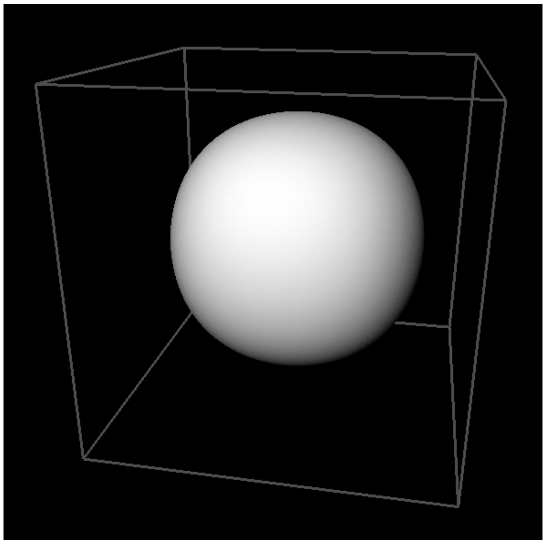

Figure 3. Six planes added on the exponential scale forming a sphere with C = e^2 with $-1.5 < x,y,z < 1.5$.

Crystal morphology

Crystals constitute the most well-ordered material in the solid state. The structure of a macroscopic crystal can be described by a periodic translation of its smallest unit cell, which typically has a size of around 1 nm. This small unit represents a formidable reduction of data; it is the sole information one needs to describe and understand a crystal structure, because it repeats with translation periodicity. Also, the morphology of a crystal is controlled by the structure, and this results in crystals having planar and sharp outer boundaries in the form of polyhedrons.

One of the characteristics from exponential scale mathematics is that most objects can be described by combinations of planes. Before going into crystal structures, we, therefore, introduce the fundamentals of the mathematics by building the morphology of crystals because they are so obviously constructed by planes.

The function $x = 10$ is in three dimensions a plane parallel with the *yz* plane, and $y = 10$ is a plane parallel with the *xz* plane. If we want to add these planes and let them continue smoothly into each other, without intersections or singularities, we can add them exponentially, as in eq 1

$$10^{x} + 10^{y} = \mathrm{C} \tag{1}$$

The constant, C, is the value for which this implicit function is displayed. The lower the value is, the closer to the origin the planes are; the higher it is, the further away they are and the sharper the intersection will become. With C = 10^{10}, the two planes meet smoothly as in Figure 1. More planes can be added in the same manner. In eq 2, we have added four more terms, which describes the cube in Figure 2.

$$10^{x} + 10^{y} + 10^{z} + 10^{-x} + 10^{-y} + 10^{-z} + = \mathrm{C} \tag{2}$$

The higher the value of the constant, the sharper the cube gets and, at a low constant value, the planes will affect each other more, which will give a more spherical object. With C = e^2, eq 2 leads to a beautiful sphere (Figure 3).

With these types of functions, all crystal morphologies can be described [17]. The different planes are simply added on the exponential scale, generating a unique mathematical equation for the polyhedrons. We can use the *law of addition* to derive analytical functions corresponding to more and more sophisticated objects. The exponential function works as a mathematical “glue.”

Crystal structures

By periodically repeating the planes in the polyhedrons using trigonometric functions, crystal structures are formed. In this section, we would like to show how very simple equations allow one to visualize the basic packings and how the combination of partial structures, that is, partial equations, leads to the most intricate structures. The following equations in this section can easily be plotted with classical mathematical software applications such as Mathematica or Maple, running on a personal computer. Starting from the equations provided, the students can generate the structures in three dimensions,

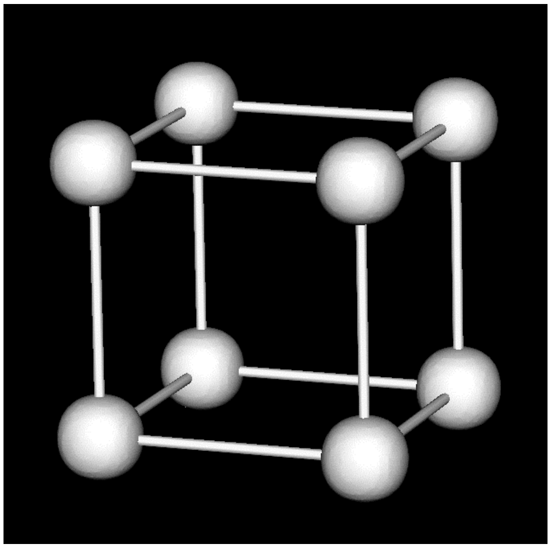

Figure 4. Primitive cubic-packing. C = 1.3 with $-0.75 < x,y,z < 0.75$.

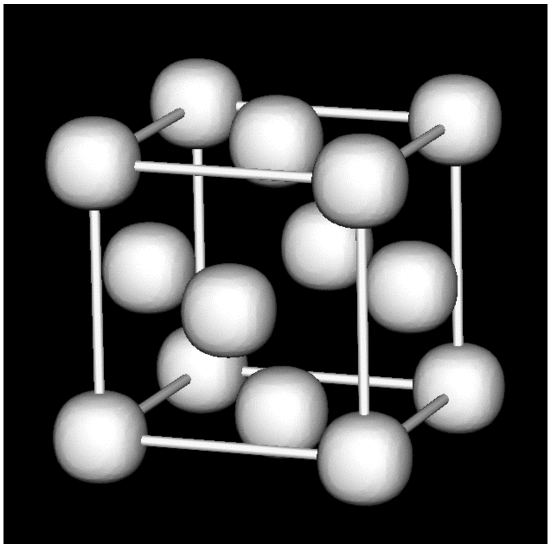

Figure 5. Face-centered packing. C = 0.6 with $-0.75 < x,y,z < 0.75$).

rotate them to have a better feeling of the space organization, and, most importantly, learn by themselves that the very complicated structures can be easily "dismantled" into more simple components as demonstrated in this section for the perovskite structure.

We start by periodically repeating the sphere with the cosine function, and now use the base e instead of 10. We only use the positive terms from the sphere, as in eq 3

$$e^{\cos(2\pi x)} + e^{\cos(2\pi y)} + e^{\cos(2\pi z)} = C \tag{3}$$

This equation results in the primitive cubic packing (cP) of atoms, as seen in Figure 4 (the cell edges have been added and are not part of the surface).

Now, playing with this exponential scale, we can derive the fundamental cubic symmetries and start to build more complex structures by using the law of addition. In order to keep equations as simple as possible, we will take advantage of the trigonometric relationships and use mainly products of trigonometric functions, although several equations may correspond to the same packing. For instance, eq 3 gives a cP packing with a cell parameter, the repeating distance, equal to 1. A similar result is obtained with

$$e^{\cos(2\pi x)+\cos(2\pi y)+\cos(2\pi z)} = C \tag{4}$$

or

$$e^{\cos^2(\pi x)\cos^2(\pi y)\cos^2(\pi z)} = C \tag{5}$$

Thus, the simplest function we will use to derive the equations corresponding to the structures we are looking for is

$$e^{\cos(2\pi x)\cos(2\pi y)\cos(2\pi z)} = C \tag{6}$$

This exponential function will be our building block.

If we plot eq 6, we get, for C = 0.6, a beautiful drawing of the cubic face-centered (cF) packing. One unit cell is shown in Figure 5. It is useful to note that a phase shift in eq 6 gives a shift of the atoms without changing the structure. For example, a phase shift from $\cos(2\pi x)$ to $-\cos 2\pi x$,

$$e^{-\cos(2\pi x)\cos(2\pi y)\cos(2\pi z)} = C \tag{7}$$

results in a shift of 1/2 along a cell edge. Changing $\cos 2\pi x$ to $\sin 2\pi x$,

$$e^{\sin(2\pi x)\cos(2\pi y)\cos(2\pi z)} = C \tag{8}$$

results in a shift of 1/4 along the x axis, and setting all trigonometric functions to sine terms,

$$e^{\sin(2\pi x)\sin(2\pi y)\sin(2\pi z)} = C \tag{9}$$

gives a shift of ¼, ¼, ¼ in x, y and z. The only consequence of these phase shifts is a shift of the unit cell origin. Obviously, there is no change in the structure. The interesting point is that each exponential term can be viewed as the generator of a partial structure and, thus, the addition of several exponential terms allows one to demonstrate the basic relationships between different packings and to generate complicated structures. We can use our building block, shift it and add it to other building blocks, to create desired packings. For instance, the primitive cP packing can be described as the interpenetration of two cF packings shifted by $a/2$; thus, the cP equation can also be written as the sum of eqs 6 and 7

$$e^{\cos(2\pi x)\cos(2\pi y)\cos(2\pi z)} + e^{-\cos(2\pi x)\cos(2\pi y)\cos(2\pi z)} = C \tag{10}$$

which is equivalent to eq 5.

One of the most important structures in solid-state chemistry is the diamond structure. It can be described as the interpenetration of two cF networks, for which one is shifted by ¼, ¼, ¼.; thus, the diamond equation is generated by the sum of eqs 6 and 9

$$e^{\cos(2\pi x)\cos(2\pi y)\cos(2\pi z)} + e^{\sin(2\pi x)\sin(2\pi y)\sin(2\pi z)} = C \tag{11}$$

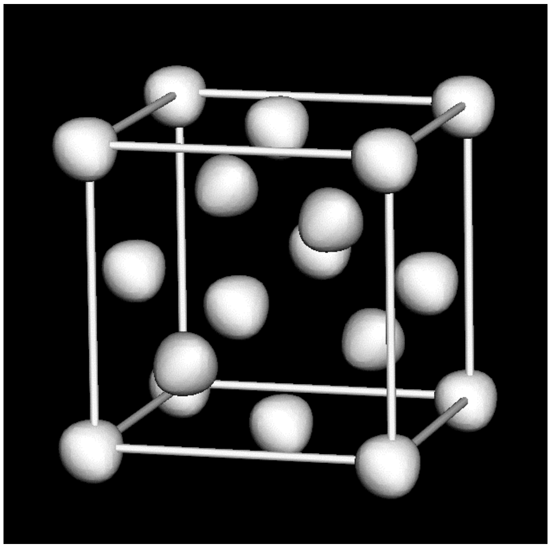

Figure 6. The diamond structure. C = 3.2 with $-0.87 < x,y,z < 0.37$).

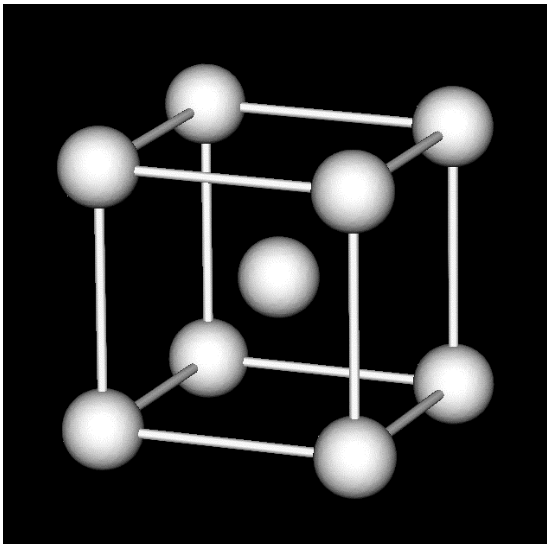

Figure 7. Body-centered-cubic packing. C = 3.2 with $-0.36 < x,y,z < 0.36$.

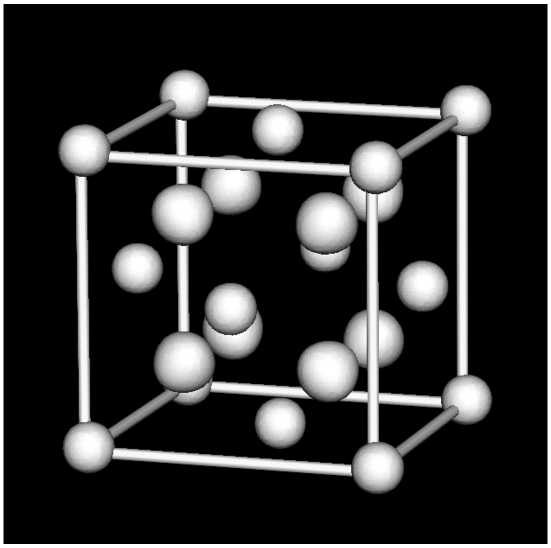

Figure 8. The CaF_2 fluorite structure. C = 2.9 with $-0.1 < x,y,z < 1.1$.

The corresponding structure is pictured in Figure 6. Introducing coefficients in the exponentials allows selective changing of the sizes of different sets of atoms. This is done in eq 12, which leads to the zinc blende structure, that is, cubic ZnS,

$$e^{1.2\cos(2\pi x)\cos(2\pi y)\cos(2\pi z)} + e^{0.9\sin(2\pi x)\sin(2\pi y)\sin(2\pi z)} = C \qquad (12)$$

Using the same strategy, affecting a phase shift by changing cosine to sine in eq 5 results in a cP cell shifted by ½, ½, ½. Two interpenetrating cP packings shifted by this vector lead to a cubic body-centered (cI) packing, for which the equation is:

$$e^{\cos^2(2\pi x)\cos^2(2\pi y)\cos^2(2\pi z)} + e^{\sin^2(2\pi x)\sin^2(2\pi y)\sin^2(2\pi z)} = C \qquad (13)$$

A cI unit cell is pictured in Figure 7. As for the zinc blende structure, the atom sizes can be changed selectively and eq 14 gives the well-known CsCl structure,

$$e^{1.2\cos^2(2\pi x)\cos^2(2\pi y)\cos^2(2\pi z)} + e^{0.9\sin^2(2\pi x)\sin^2(2\pi y)\sin^2(2\pi z)} = C \qquad (14)$$

It is of interest to note that the function $e^{\cos(2\pi x)\cos(2\pi y)\cos(2\pi z)}$ gives a cell parameter that is twice the size corresponding to the function $e^{\cos^2(2\pi x)\cos^2(2\pi y)\cos^2(2\pi z)}$. This fact can be used to build a more complex structure. The CaF_2 fluorite structure can be described with two interpenetrating networks: one cF of calcium cations with a cell parameter *a* and one cP of fluorine anions shifted by ¼, ¼, ¼ with a cell parameter $a' = a/2$. The equation for this is

$$e^{0.75\cos(2\pi x)\cos(2\pi y)\cos(2\pi z)} + e^{\sin^2(2\pi x)\sin^2(2\pi y)\sin^2(2\pi z)} = C \qquad (15)$$

Figure 8 illustrates this beautiful structure. If the coefficient, 0.75 in the first term is set to 1, the antifluorite structure (permutation of cations and anions) is obtained.

Finally, we will illustrate the power of the law of addition with one of the most famous structures, perovskite, $CaTiO_3$. Hundreds of compounds with remarkable physical properties crystallise with this structure. Three sets of atoms form the structure, titanium atoms are located at the cube corners, surrounded octahedrally by oxygen atoms that lie in the middle of the cell edges, and finally the calcium atom is situated in the center of the cubic cell. Titanium and oxygen alone form a ReO_3 network. Equation 16 gives the oxygen network,

$$\begin{aligned} &e^{\sin^2(2\pi x)\cos^2(2\pi y)\cos^2(2\pi z)} + e^{(\cos^2(2\pi x)\sin^2(2\pi y)\cos^2(2\pi z)} \\ &+ e^{\cos^2(2\pi x)\cos^2(2\pi y)\sin^2(2\pi z)} = C \end{aligned} \qquad (16)$$

The titanium atoms are then obtained in eq 17 by adding the all-cosine term to the function in eq 16,

$$\begin{aligned} &e^{\sin^2(2\pi x)\cos^2(2\pi y)\cos^2(2\pi z)} + e^{\cos^2(2\pi x)\sin^2(2\pi y)\cos^2(2\pi z)} \\ &+ e^{\cos^2(2\pi x)\cos^2(2\pi y)\sin^2(2\pi z)} + e^{\cos^2(2\pi x)\cos^2(2\pi y)\cos^2(2\pi z)} = C \end{aligned} \qquad (17)$$

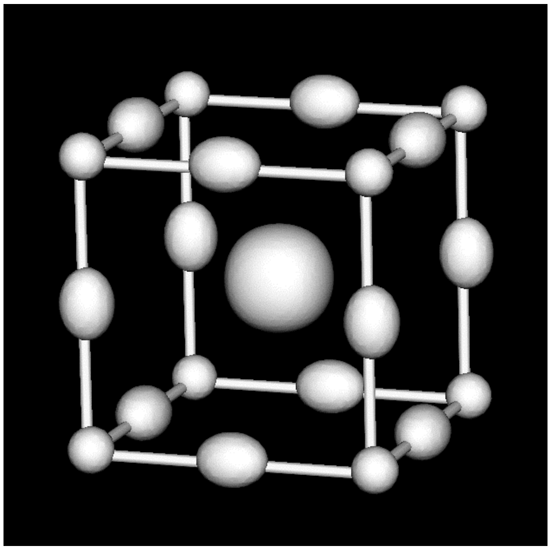

Figure 9. The perovskite structure. C = 6.5 with $-0.1 < x,y,z < 0.6$.

and this builds up the ReO_3 structure. Finally, adding a fifth all-sine term and introducing coefficients to selectively change the atom sizes, we get the full perovskite structure with eq 18,

$$\begin{aligned}&e^{\sin^2(2\pi x)\cos^2(2\pi y)\cos^2(2\pi z)}+e^{\cos^2(2\pi x)\sin^2(2\pi y)\cos^2(2\pi z)}\\&+e^{\cos^2(2\pi x)\cos^2(2\pi y)\sin^2(2\pi z)}+e^{0.95\cos^2(2\pi x)\cos^2(2\pi y)\cos^2(2\pi z)}\\&+e^{1.3\sin^2(2\pi x)\sin^2(2\pi y)\sin^2(2\pi z)}=C\end{aligned}\tag{18}$$

The structure is pictured with C = 6.5 in Figure 9.

In our teaching experience, it is always difficult for the students to see the spatial atomic organization if a structure is a little bit more complicated than NaCl for example. The mathematics described in this section offers the unique possibility to built step-by-step complicated structures starting from the most simple packings of atoms. Other equations corresponding to cubic and hexagonal structures are given in the appendix at the end of this paper. In addition, instructors can easily built their own examples. Moreover, students show a strong tendency to consider the structural chemistry as a collection of strange animals, each of different species. Exponential mathematics offers the possibility to give evidence of the relationships between different structures, for example the equations of diamond; zinc blende, ZnS; and cristobalite.

Dynamical Structure Descriptions. Structure–Property Relationships

The functions given above all represent atomic packings of crystal structures, and the way of constructing them by adding different partial structures can be useful in the tough work of teaching structural chemistry. They also can help to generate a much deeper understanding of crystal structures by varying the isosurface constant, C. This constant represents a kind of fourth dimension in the structures and, therefore, the structures become dynamic. Each equation consists of an infinite number of isosurfaces, for which we, so far, have only displayed the atom-like ones. By scanning the constant, it is possible to continuously follow the structure from small ball-shaped atoms, let them grow to reach packings of interconnected polyhedrons, and then further to dividing minimal-like surfaces. These surfaces are useful tools for at least three applications. They constitute a powerful unifying tool in solid-state chemistry as they allow a simple and unique description of different complex structures in different fields (metallic alloys, oxides, etc.). These surfaces can also be used to understand the atomic interactions in the structures. Finally, they are an efficient tool to explain structure–property relationships.

Still, the first interest of this concept is that a much clearer understanding of the structure can be reached by this description. We will demonstrate this for the case of diamond packing, eq 11. Figure 10 represents the surface calculated for different values of the isosurface constant. The cubic boundary in this figure is the space in which the function is calculated, and it should not be confused with the crystallographic unit cell. In 10a, the constant is 1.38, and the surface corresponds to a classical “ball” view of the packing. Increasing the constant makes the balls larger until they meet each other and connect through catenoids at C = 1.41, resulting in the representation of the structure as a bond network in Figure 10b. For a constant of 2.0 in 10c, the size of the balls is greatly increased and they merge into each other forming large catenoidic channels. The structure here forms a continuous dividing surface, an analog to a minimal surface called the D surface. For a constant equal to 2.84 in Figure 10d, we obtain corner-connected tetrahedrons, and at C = 3.6 in Figure 10e, we again get a diamond packing, but this one resides on the other side of the D surface (compare the atomic positions in Figures 10a and 10e). Figure 11 gives an enlarged view, showing the symmetry of the D surface that separates the two interpenetrating diamond structures.

This demonstrates a general property of minima-like surfaces—they are space partitioners; they split space into two interpenetrating domains. The dynamic description of a structure generates a better and more correct description of the actual structure and gives a feeling for the forces and open spaces present. This new way of visualising the structures is probably the main benefit of this mathematical approach. First, a particular surface allows one to describe a series of structures with the same topology. For example, the D surface, used to describe the diamond structure, also corresponds to metallic alloys, such as the γ-brass related structure, $Li_{21}Si_5$; or the Laves phase, $MgCu_2$; or to the extremely complicated zeolite, faujasite. The P surface, which corresponds to a primitive cubic packing (eq 3, Figure 12), allows a common description of CsCl; α-Mn; the tungsten bronze, Na_XWO_3; and the zeolite, Linde A, among many other structures. Numerous examples are given in references 8 and 10. For many purposes, a precise description using atomic positions is not necessary. For example, in the case of the complicated structures of zeolites, it is often sufficient to show the topology of the cages and tunnels to explain the chemical and physical properties. The description in term of minima-like surfaces is a very useful tool.

In other cases, the coexistence of two descriptions, atomic positions and surface, is extremely fruitful. Taking again the example of the zeolites, Linde A and faujasite, the comparison of the atomic positions with the corresponding surface shows that the aluminosilicate network fits onto the surface, whereas the exchangeable cations and water molecules lie in the

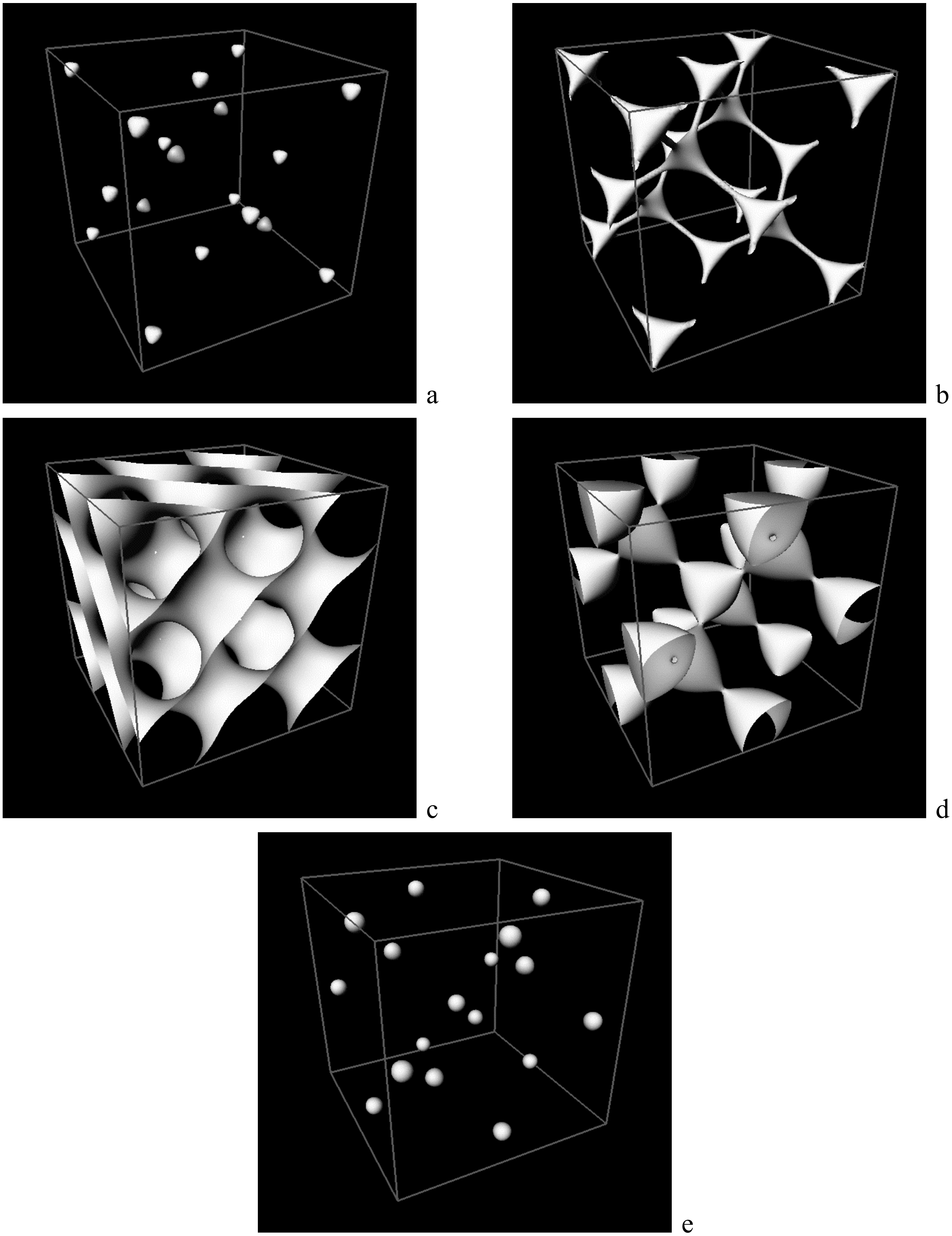

Figure 10. (a) Diamond packing, C = 1.38 with $-0.6 < x,y,z < 0.6$); (b) network of tetrahedra connected via catenoids, C = 1.41; (c) the D surface analog, C = 2.00; (d) corner-connected tetrahedra, C = 2.84, on the other side of the D surface; (e) diamond packing, again, with C = 3.6; this one interpenetrating the first one shown in Figure 10a.

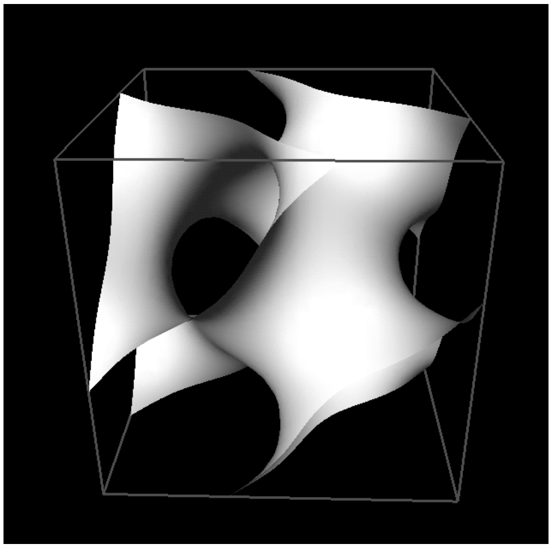

Figure 11. Enlargement of the D surface.

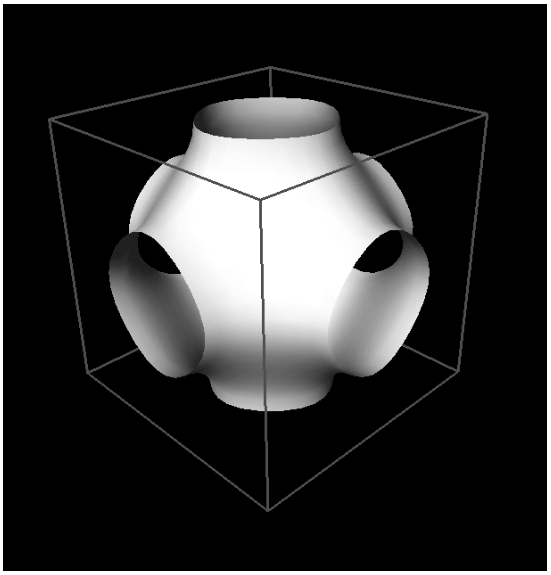

Figure 12. Enlargement of the P surface.

tunnels or the cages. Moreover, the oxygen atoms of the network are coordinated in such a way that the lone pairs point towards the cations on both sides of the surface [10], accounting for the polar interactions.

This concept of surfaces acting as space partitioners is extremely powerful to illustrate structure–property relationships. One of the best examples is the problem of the conduction paths in fast-ion conductors [8,20]. The very good ionic conductor, α-AgI, is known to crystallize with a bcc "immobile" array of iodine anions and disordered silver cations. The anions are situated on both sides of the minimal surface P. The cations, ensuring conductivity, move along trajectories fitting onto the surface. This is the best route in term of charge considerations because the largest potential gradients are always perpendicular to the surface. By definition, there is no potential gradient along a minimal surface. The same conclusions can be drawn for other ionic conductors, such as PbF_2; partially stabilized zirconia; or β-eucryptite, $Na_XAl_2O_3$ [10]. Phase transitions can also be explained in the light of the minimal surfaces. The martensitic transformation in steel is always difficult to teach. The classical view of this transition is the Bain mechanism. Crystallographically the transformation is from fcc austenite to bcc martensite. It involves a 17% compression along one axis and a 12% expansion along the two other axes. The transformation is characterised by a drastic atomic rearrangement, a macroscopic shape change, a very high velocity, and an orientational relationship between the austenite and the resulting martensite. This mechanism is widely acknowledged because it gives an excellent agreement with the experimental results, but it is unable to explain the real movements of the atoms during the transformation. The austenite and martensite structures can be described with minimal-like surfaces, the D surface and the gyroid surface, respectively. In both structures, iron atoms are fixed on the flat points of the surface. The martensitic transformation can be described as a continuous bending from the D surface to the gyroid surface in such a way that iron atoms remain on the flat points and all intermediate structures are themselves minimal surfaces [7]. Other examples of phase transitions can be found in ref 10 and references therein

Readers interested in learning more about the mathematics of minimal surfaces may explore different Websites to get images and bibliography. One of the best is the site of the Scientific Graphics Project, headed by David Hoffman, at the Mathematical Sciences Research Institute, Berkeley [21]. Pedagogical short texts and magnificent images are given. A very complete bibliography, particularly papers by D. Hoffman, is available [22]. The site of the Institute of Physical Chemistry in Warsaw (Poland) [23] presents beautiful enlargements of the most known surfaces (P surface, diamond, gyroid, etc.) and gives references to interesting applications in the field of microemulsions, surfactants, and block copolymers. Other geometry resources on the World Wide Web can be found on the mentioned sites.

Using Exponential-Scale Mathematics with Students

This method of teaching crystal structures has been tested at the Universities of Geneva (Switzerland) and Grenoble (France) with students in their second and third years [24].

The only prerequisite is a normal knowledge of the exponential and trigonometric functions. The mathematics of periodic minimal surfaces is not needed, but the concept of equipotential surfaces is useful. Before applying exponential-scale mathematics to crystal structures, students have been trained to use Maple, which takes a relatively short time as the programming-language is simple and the plot of 3D-surfaces is preprogrammed in the software application. The short program used to draw Figure 5, using eq 6, is given as an example in reference 25.

In a first step, students work on very simple equations, as eqs 1 and 2, in order to understand that the exponential function acts as a glue between several objects and to see the effect of the constant value on the final object. Then, starting with eq 3 (the necessity of using trigonometric functions to get a periodicity is obvious for the majority of the students), the students learn the consequences of introducing a phase shift (from $\cos(2\pi x)$ to $-\cos(2\pi x)$ or $\sin(2\pi x)$, for example) and using a multiple angle (from $\cos(2\pi x)$ to $\cos(4\pi x)$, for

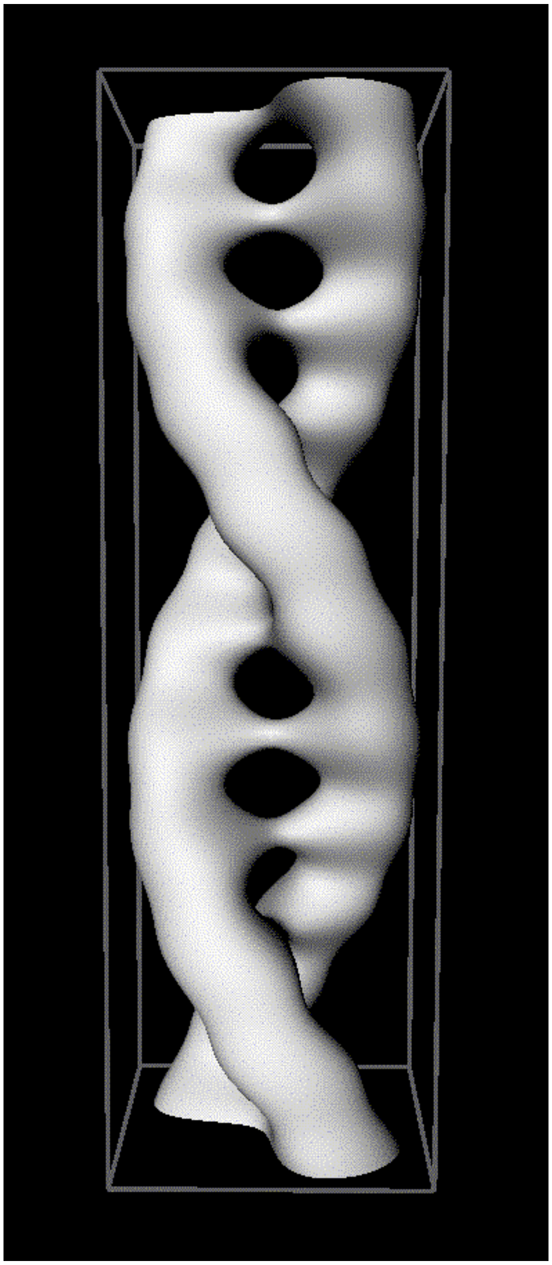

Figure 13. The DNA double helix with its bridging hydrogen bonds.

example), as they apply to atomic positions and cell parameters.

The second step sheds light on the notion of a subnetwork. There are three objectives: to built the most important basic structures and to create a good 3-D vision of these structures, to give evidence of the relationships between different structures (see eqs 11 and 22, for example), and to connect two descriptions that are traditionally separated: the packing of atoms (ball-and-stick) and the packing of polyhedrons. In our experience, this last step is always the limiting one if structural chemistry is taught with pictures and plastic models. This is true for two reasons: (1) it would cost a fortune to built all the models necessary to demonstrate these points and (2) the students usually do not have enough time to manipulate the models. Thus, it is very often difficult to go on when the knowledge corresponding to this step is not well assimilated. With our mathematics, provided that the software application is in readily accessible, the students make their own models, which they can rotate in 3D, modify, and print to compare with the textbook. All figures given in this paper represent one unit cell; obviously, it is possible to draw larger packings of atoms simply by enlarging the space in which the function is calculated; however, larger packings are more difficult for students to understand. Other programs enable the viewing of 3-D structures on the computer (i.e., CrystalMaker and Ortep) and the drawing of more sophisticated pictures. Still, very often, they are not easy to use by students (Ortep) and not readily available, whereas Mathematica or Maple are available in many departments. Moreover, programs like Ortep work with atom coordinates and only give the classic ball-and-stick representation.

In a third step, the concept of a periodic minimal surface is introduced very pragmatically as demonstrated by Figure 10. The complex mathematics used to study the PMS is completely transparent in this approach. Two main objectives for this step are:

- to show that a particular surface corresponds to different structures and, thus, can be used to describe very complex structures that, otherwise, would be incomprehensible to the student. (For example, P and D surfaces, which are relatively easy to see, can be used to introduce the structural chemistry of zeolites.)
- to illustrate structure–property relationships. (A number of excellent textbooks explain the mechanism of conduction in fast ionic conductors [26]. Still, in our teaching experience, even the most intelligent students fail to understand the mechanism when looking at the ball-and-stick structure of β-alumina, for example. We think that it is much easier to understand the problem of conduction paths looking at the minimal-like surface corresponding to the structure. In this part of the work, surfaces must be precalculated (or taken from the literature) and given to the students. Otherwise, it takes them too much time.)

Finally, we would like to emphasise again that the complex mathematics of PMS are not needed to use our method. PMS is a teaching tool that is much more efficient that ball-and-stick models. Of course, if the students have a good knowledge in crystallography, this approach can be linked to a description based on symmetry elements and space groups (see refs 11 and 27).

Conclusions and Extensions

The exponential scale functions allow us to build up crystal structures by adding different building blocks, just like we do when building plastic models. The result is a single analytical mathematical function describing the structure. A further strength of such a description is the dynamic behavior revealed when scanning the isosurface constant. This way a more thorough understanding of the structures can be obtained, and the connection between different types of traditional descriptions (ball models, polyhedral models, bond networks, minimal surfaces, rod packings etc.) is better understood.

There are many extensions for this type of mathematics. It allows for the combination of different types of geometry, creating forms that otherwise are not possible to describe with single mathematical functions. Finite periodic functions that

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also contain external outer boundaries and describe finite objects can be made. For instance, it is possible to add the D surface to outer boundaries shaped as an octahedron to create a cubosome, which is a lipid bilayer formation [28]. Also, isolated molecules can be created and later combined. Using other functions, for instance the Gaussian distribution, e^{-x^2}, it is possible to hand-make structures by placing isolated balls at positions of choice.

Finally, to illustrate how powerful this mathematical approach is, the DNA double helix can be modelled by the following equation

$$\begin{aligned} &xy\cos(\tfrac{\pi z}{10})+\tfrac{1}{2}(x^2-y^2)\sin(\tfrac{\pi z}{10}) \\ &-\cos(\tfrac{\pi z}{2})+\tfrac{3}{5}e^{(x^2+y^2)/10}=0 \end{aligned} \tag{19}$$

This equation generates the structure in Figure 13, which shows one pitch of the DNA double helix with its ten base pairs and their bridging hydrogen bonds. The two first terms in eq 19 create a double helicoid, the third generates saddles in this, and the last term is a cylinder exponentially added to close up the surface to the double helix [19].

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Appendix: More Equations

Below we give the equations of several well-known structures that should help the reader to understand the principle of the law of addition. We refer to classical textbooks, such as *Structural Inorganic Chemistry* [29] for the corresponding structure illustrations.

1 Cubic structures. *1.1 Sodium chloride, NaCl*

$$e^{\cos(2\pi x)\cos(2\pi y)\cos(2\pi z)}+e^{1.5\cos^2(2\pi x)\cos^2(2\pi y)\cos^2(2\pi z)}=3.2 \tag{20}$$

1.2 Magnesium fluoronitride, Mg_3NF_3

$$\begin{aligned} &e^{\cos(2\pi x)\cos(2\pi y)\cos(2\pi z)}+e^{1.5\cos^2(2\pi x)\cos^2(2\pi y)\cos^2(2\pi z)} \\ &-(e^{\cos^2(2\pi x)\cos^2(2\pi y)\cos^2(2\pi z)}+e^{\sin^2(2\pi x)\sin^2(2\pi y)\sin^2(2\pi z)}) \\ &=0.75 \end{aligned} \tag{21}$$

The structure of Mg_3NF_3 is a defect NaCl structure. Magnesium atoms lie on the face centers, fluorine atoms on the middle of the cell edges, and the nitrogen atom at the center of the cubic cell. Thus, the cube corners are not occupied. In eq 21, the first two terms correspond to the true NaCl structure and the two last terms to the “missing” atoms.

1.3 Cristobalite, SiO_2

$$\begin{aligned} &e^{1.2\cos(2\pi x)\cos(2\pi y)\cos(2\pi z)}+e^{1.2\sin(2\pi x)\sin(2\pi y)\sin(2\pi z)} \\ &+e^{\cos^2(4\pi x)\cos^2(4\pi y)\cos^2(4\pi z)}+e^{\sin^2(4\pi x)\sin^2(4\pi y)\sin^2(4\pi z)} \\ &=3.8 \end{aligned} \tag{22}$$

Cristobalite is one of the three natural forms of silicon oxide, along with quartz and tridymite.

1.4 Ordered Cu_3Au alloy

$$e^{\cos^2(2\pi x)\cos^2(2\pi y)\cos^2(2\pi z)}+e^{\cos(4\pi x)\cos(4\pi y)\cos(4\pi z)}=2.6 \tag{23}$$

2 Hexagonal Structures. Obviously, the use of the exponential scale is not restricted to cubic structures. We just used the cubic symmetry for simplicity, but we have also derived equations for the most well-known hexagonal structures.

2.1 Primitive hexagonal packing

$$e^{\cos(2\pi x)\cos(2\pi\sqrt{3}y)\cos^2(2\pi z)}=0.7 \tag{24}$$

2.2 Hexagonal close-packing (hcp)

$$\begin{aligned} &e^{\cos(2\pi x)\cos(2\pi\sqrt{3}y)\cos^2(2\pi z)} \\ &+e^{\cos(2\pi(x+1/3))\cos(2\pi\sqrt{3}y)\sin^2(2\pi z)}=1.5 \end{aligned} \tag{25}$$

In order to obtain the hcp cell with the ideal *c*/*a* ratio, a coefficient $2\sqrt{2}/\sqrt{3}$ must be introduced in the *z* terms.

2.3 NiAs structure

$$\begin{aligned} &e^{1.1\cos(2\pi x)\cos(2\pi\sqrt{3}y)\sin^2(2\pi z)}+e^{\cos(2\pi(x+1/3))\cos(2\pi\sqrt{3}y)\cos^2(\pi z)} \\ &+e^{\cos(2\pi(x-1/3))\cos(2\pi\sqrt{3}y)\sin^2(\pi z)}=3.9 \end{aligned} \tag{26}$$

2.4 ZnS Wurtzite structure

$$\begin{aligned} &10^{\cos(2\pi x)\cos(2\pi\sqrt{3}y)\cos^2(2\pi z)}+10^{\cos(2\pi(x+1/3))\cos(2\pi\sqrt{3}y)\sin^2(2\pi z)} \\ &+10^{\cos(2\pi x)\cos(2\pi\sqrt{3}y)\cos^2(2\pi(z+0.19))} \\ &+10^{\cos(2\pi(x+1/3))\cos(2\pi\sqrt{3}y)\sin^2(2\pi(z+0.19))}=11.5 \end{aligned} \tag{27}$$

The structure can be described as the interpenetration of two hcp networks shifted by 0.38 along the *c* axis.

2.5 Graphite structure

$$\begin{aligned} &10^{\cos(2\pi x)\cos(2\pi\sqrt{3}y)\cos^2(\pi z)}+10^{\cos(2\pi(x+2/3))\cos(2\pi\sqrt{3}y)\cos^2(\pi z)} \\ &+10^{\cos(2\pi(x+1/3))\cos(2\pi\sqrt{3}y)\sin^2(\pi z)} \\ &+10^{\cos(2\pi(x-1/3))\cos(2\pi\sqrt{3}y)\sin^2(\pi z)}=9 \end{aligned} \tag{28}$$

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25. The Maple program corresponding to Figure 5 can be written as follows:

```
restart:
p:=2*3.1416;
a:=cos(p*x)*cos(p*y)*cos(p*z);
c:=exp(a);
with(plots):
implicitplot3d(c=0.6,x=-0.75…0.75,y=-
0.75…0.75,z=-0.75…0.75);
Options  allows  one  to  control  axes,
orientation, shading, colours, etc…
```

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