

Calculation of surface enthalpy of solids from an ab initio electronegativity based model: case of ice

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Abstract

A very simple route to calculation of the surface energy of solids is proposed because this value is very difficult to determine experimentally. The first step is the calculation of the attractive part of the electrostatic energy of crystals. The partial charges used in this calculation are obtained by using electronegativity equalization and scales of electronegativity and hardness deduced from physical characteristics of the atom. The lattice energies of the infinite crystal and of semi-infinite layers are then compared. The difference is related to the energy of cohesion and then to the surface energy. Very good results are obtained with ice, if one compares with the surface energy of liquid water, which is generally considered a good approximation of the surface energy of ice.

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1. Introduction

Since the pioneering work of Frenkel [1], it has been clear that the surface tension of solid and liquid phases, in the presence of vapor or vacuum, is directly related to the structure of the sublayer phase and to the strength of the chemical bonds ensuring the cohesion of the condensed phase. Equations have been proposed to calculate either the surface enthalpy from bulk characteristics such as the enthalpy of vaporization, or the surface entropy from a numeration of empty spaces inside the surface layer [2–13].

But, in the details, such calculations, interesting a priori, were deceptive in their realization. One of the reasons is the impossibility of determining without assumption how many “layers” are composing the surface phase [14]. Indeed, in such models, generally called “broken bonds models,” the bulk is divided into homogeneous layers and a certain number of layers are attributed to the surface phase. Some defects are introduced into these surface layers [4], and the computation is performed. But, in surface thermodynamics, the surface phase is definite as an “excess phase,” of which the volume characteristics are not known precisely. Then,

if it is possible to understand in outline the behavior of a surface phase and to predict the surface tension or the surface enthalpy, this implies assumptions, which in fact are related to an unjustifiable choice of surface thickness [15,16].

And this situation arises in the most favorable case, i.e., in the case of a liquid phase composed of a single species. In the case of mixtures, some supplementary assumptions are necessary. These assumptions are realistic because, if the mixture is effective, that implies some similarities between species constituting it. Then it is possible to consider the liquid as a pure phase, slightly modified by a single parameter, the activity coefficient. And at the molecular level, one can consider that the liquid is homogeneous. However, for solid phases composed of different species, the situation is more complex. Of course, some solids are unary or binary, but this is generally only the case in the bulk. Surfaces of solids are often generated by mechanical ruptures, which create chemical modifications [17]. It is then generally true that the bulk composition and the surface composition are very different. The most classical example is the case of silica, which is composed of Si and O atoms, but where the surface generally bears SiOH groups [18]. Moreover, some surface electrical charges can appear [19], or some contamination. And finally, even though it is very easy to define structural “layers” inside a solid bulk structure, it is very difficult to de-

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fine similar layers at the surface. Neither the composition nor the arrangements are identical in the bulk and in the surface, looking at a solid.

Since the progress of computers and the development of theoretical chemistry, some other numerical routes have been proposed in order to calculate the surface energies of solids from the energy characteristics of solid network bonds [20–22]. But three other problems have appeared. First, surface energy characteristics of pure solids determined from experiments are few [23–25]. Second, the computations of interactions between a solid phase and an adsorbing species, which conclude the computations of surface energies of solids, are generally compared to “differential energies of adsorption” or to contact angles [26], which do not take into account pure solid characteristics. (It is true that in some cases, values extrapolated “at zero coverage” are used, which theoretically take into account the surface energy of the bare solid, but these extrapolations are poorly precise and thus the success of the computation is difficult to determine.) Thus, interpretations are poor. Third, computation routes proposed are often very complex and many different parameters are used, which generate results that are difficult to compare with experiments [27]. And thus, a general view of the calculation of surface energies is still lacking.

In this paper, we propose to use a simple computation method, recently developed by one of us [28], in order to compute surface enthalpy of solids. This route uses the general theory of electronegativity and hardness [29,30]. The necessary numerical parameters attributed to the pure components are chosen because they have a clear physical meaning. The computation starts when the different positions of the atoms inside the solid network are available. A computation of the electrostatic part of the bond energy of the unit structure is then possible [5]. A similar computation, but only concerning chosen parts of the structure, is also possible, and then it is easy to calculate this energy for layers of the structure. The difference of energy between the layer and the bulk can be attributed to the energy of cohesion of the structure, and thus the surface enthalpy can be estimated. We present here results obtained for ice, because liquid water is a species for which it is possible to determine the surface enthalpy experimentally, and because surface enthalpy is expected to vary only slightly between water and ice when the composition is kept constant [14,31].

2. Thermodynamic background

2.1. Surface free energy

A surface is defined as a geometrical part of space, located between two condensed phases. Generally, the composition of surface is different from the bulk compositions. One can consider that a bulk is homogeneous, whereas a surface is heterogeneous, considering a direction of the space per-

pendicular to the surface of division between the two condensed phases. Some work is necessary to increase a surface area. If G^S is the Gibbs free energy of the surface, the part of this free energy necessary to increase or decrease the surface area A is denoted as γ , the surface tension, defined as

$$\gamma = \left(\frac{\partial G^S}{\partial A} \right)_{T,P,n}. \quad (1)$$

The subscripts T , P , and n specify that pressure, temperature and composition (in the surface phase) remain constant during the process. The total free energy of a surface without stress can then be written

$$G^S = \sum_i n_i \mu_i + A\gamma. \quad (2)$$

The other surface energies (U^S , H^S) follow immediately. Surfaces can be considered as very thin and then the dV term is negligible. Then we have $H^S \approx U^S$. The surface tension of solids has to be defined precisely [32,33]. Indeed, considering a solid, the stretching of the surface and the forming of a new surface are different processes. The solid surface tension in the vacuum (γ_S ; the subscripts correspond to the bulk phases in contact) is the derivative of the free energy associated with the formation of a new surface in the vacuum. There is an equivalent term associated with the stretching of a surface, which is called the surface stress Υ . A generalized surface intensive parameter can be defined from the surface tension and the surface stress. But, generally, surface phenomena are studied and are relevant in the absence of strains applied to the solid. Therefore, this is the surface tension, which is relevant. Generally, the superscript o is added to indicate that the solid surface tension is defined in absence of strain (γ_S^o). However, there is no simple experience that gives the value of the surface tension of the solid.

2.2. Enthalpies

It is useful, in view of using simple equations, to define a derivative of the surface energy, denoted H_{ij} , by the following equation:

$$\left(\frac{\partial U^S}{\partial A} \right)_{T,V',V''} = H_{ij} = \gamma_{ij} - T \left(\frac{\partial \gamma_{ij}}{\partial T} \right)_{T,P}. \quad (3)$$

This term corresponds to the total energy of extension of the interface between phases i and j , per unit increase in area. It is generally called the “surface enthalpy,” even though it is clearly (i) a derivative and consequently (ii) an intensive term. It is generally the characteristic term needed discussing surface energy of condensed phases. Obviously, in the case of solids, it is a term related to γ_S^o and thus does not take into account the effect of strain. Then, it could be an insufficient term to describe solid surfaces where strain effects are important. At a first level of approximation, we will assume that this term is sufficient in the experimental case described

below and we will use the definition of surface enthalpy corresponding to Eq. (3). Like the surface tension of solids, the surface enthalpy of solids is very difficult to estimate experimentally. However, when dealing with pure phases in absence of chemical reaction, it is the only enthalpic term varying during an immersion or a wetting process. Using “immersion calorimeters”, it is then possible to obtain the integral enthalpy of adsorption, $\Delta_{\text{ads}}H$, which corresponds to going from the pure solid under vacuum to the adsorbed phase. The corresponding equation is [24]:

$$\begin{aligned} \Delta_{\text{ads}}H &= (\gamma_S^o - \gamma_{\text{SV}}) - T \left(\frac{\partial(\gamma_S^o - \gamma_{\text{SV}})}{\partial T} \right) \\ &= H_S^o - H_{\text{SV}}. \end{aligned} \quad (4)$$

Some other enthalpies of adsorption, which are differential, can be measured using calorimeters. The exact definition depends on the type of experimental arrangement employed. In an isothermal volume calorimeter in which the reversible adsorption of an amount of gas, dn , is accompanied by an exchange of heat, dq , the differential heat (dq/dn) is related to a differential enthalpy, conventionally called the *isosteric enthalpy of adsorption* $\overline{\Delta_a H}$. Rigorously speaking, this term is clear when extrapolated to zero coverage, e.g. to nil pressure of the adsorbed gas. Then, it corresponds to the association of the first molecules of gas with the bare solid surface. However, when taken at a finite value of the partial pressure, it corresponds to a derivative of the enthalpy with some terms such as the chemical potential of adsorbing sites taken as constant. The reader is invited to go to more detailed books [34]. Basically, the extrapolation of differential heats at zero coverage is equivalent to the integral enthalpy of adsorption but expressed in joules per mole.

Obviously, the integral enthalpy of adsorption is a key parameter, because it can be analyzed as the energy corresponding to a reaction between two pure species: the adsorbing species and the solid [35]. It is necessary to assume that the solid is heterogeneous at the scale of the molecules but homogeneous at the scale of a mole. The adsorption energy can then be viewed as a combination of the energies of two pure species, each one composing the solid and the liquid, and used to determine the energy of the solid. One of us has recently proposed a model of calculation of the enthalpy of adsorption, by considering that the interaction enthalpy is a function of the pure species enthalpies [24]. The basic equation is the following:

$$H_{ij} \approx H_i + H_j - 2\phi\sqrt{H_i H_j}. \quad (5)$$

ϕ is a phenomenological interaction parameter.

This method uses a very general framework, which considers that the surface energy (and obviously, more generally, the bond energies) are sums of different components [36]. At first level, one can consider that a repulsive term and some attractive terms compose the energy. The repulsive term and the dispersive part of the attractive energy compose the van der Waals term of the energy. Two

other main attractive terms are acting, the polar part between dipoles and the electrostatic part between charges:

$$H^S = H^{\text{LW}} + H^{\text{AB}} + H^\pm. \quad (6)$$

Considering the interaction of solids with pure liquids, if the whole concerned phases are neutral at equilibrium, the term corresponding to electrical charges can be neglected, and then the measurement of a chosen enthalpy for liquids of different Lewis acid–base and dispersive characters gives access to the surface enthalpy. On this basis, it has been possible to calculate the surface enthalpies of some solids or, alternatively, to predict energies of adsorption or wetting [37]. But in the case of ice, we will here consider that the surface enthalpy of liquid water is an acceptable approximation [14]. This surface enthalpy can be obtained by surface tension measurements at different temperatures. In the literature, a value of 118.5 mN/m is generally accepted.

3. Broken bonds models

In physical terms, H_{ij} is the total potential energy of the molecules that forms 1 m² of the surface in excess of the energy the same molecules would possess in the bulk. Frenkel has suggested that this energy is related to the molecular cohesion of the subsurface phase. It is necessary to consider that molecular cohesion is insured by interactions between neighboring molecules in order to use simple equations. Let the number of nearest neighbors of a molecule inside the bulk phase be Z^{B} and let the number of neighbors for the molecule in the surface be Z^{S} . Then, if (N_A/\bar{V}) is the number of molecules per unit volume, and if ε_i is the mutual cohesive energy of two neighboring molecules, the surface energy per unit area is given by

$$H^S = \varepsilon_i (Z^{\text{B}} - Z^{\text{S}}) \left(\frac{N_A}{\bar{V}} \right)^{2/3}. \quad (7)$$

Some terms related to the properties of the bulk can be introduced in this equation. For example, the molar sublimation energy, which then corresponds to the energy of a solid–vapor interface:

$$\Delta_{\text{subl}}h = \frac{1}{2} N_A Z^{\text{B}} \varepsilon_i \quad \text{or} \quad \Delta_{\text{subl}}h = \frac{1}{2} Z^{\text{B}} h_i. \quad (8)$$

The factor 0.5 takes into account the fact that the removal of one molecule breaks a certain number of bonds, but the staying molecules recreate bonds. h_i is the molar mutual cohesive energy of two neighboring molecules. Then, a possible relation is

$$H_{\text{SV}}^S = \Delta_{\text{subl}}h \left(\frac{2}{N_A^{1/3} \bar{V}^{2/3}} \right) \left(1 - \frac{Z^{\text{S}}}{Z^{\text{B}}} \right), \quad (9)$$

and for a liquid–vapor interface, one gets

$$H_{\text{LV}}^S = \Delta_{\text{vap}}h \left(\frac{2}{N_A^{1/3} \bar{V}^{2/3}} \right) \left(1 - \frac{Z^{\text{S}}}{Z^{\text{B}}} \right), \quad (10)$$

where $\Delta_{\text{vap}}h$ is the enthalpy of vaporization. The obvious problem of such an equation is the number of unknown parameters. Another problem is less obvious. It is due to the observation that the energy of a “bulk layer” expressed per square meter seems very near of the surface energy, i.e., the number of broken bonds seems very low. Anyway, it is possible to estimate Z^B , but it is necessary to model the surface to estimate Z^S . To calculate this energy for the liquid–vapor interface of water, it is possible to consider one single layer. Then, it is necessary to consider that only a bond is broken in the surface for 12 bonds in the bulk ($Z^S = 1$, $Z^B = 12$). Indeed, one has $\Delta_{\text{vap}}h = 44$ kJ/mol, and a value of 118.5 mJ/m² is expected. Then, if one considers only a layer in the surface phase, surface and bulk water structures appear very similar. But the choice a priori of a realistic number of layers is very difficult. Then, the broken bonds models are not often used.

4. Computational background

Pauling has defined the term electronegativity as the power of an atom in a molecule to attract electrons. On the basis of this definition, Pauling used differences in electronegativity to estimate bond energies between heteroatomic molecules. It appeared that another concept is necessary in order to interpret the chemical bonds. This is hardness, which is the measure of resistance of a chemical species to changes in its electronic configuration. Formalization of electronegativity and hardness concepts has been carried out in the framework of density functional theory [38]. In this theory the chemical potential μ of the electrons of the studied system is the derivative of the energy, E , with respect to the number of electrons, N , at constant external potential, $v(r)$,

$$\mu = \left(\frac{\partial E}{\partial N} \right)_v. \quad (11)$$

The hardness η is then

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_v = \left(\frac{\partial \mu}{\partial N} \right)_v. \quad (12)$$

In practice, these definitions are often replaced with the following approximations relating the chemical potential and the hardness to the ionization potential and the electron affinity,

$$\begin{aligned} \mu &\approx -\frac{1}{2}(I + A) = -\chi, \\ \eta &\approx (I - A). \end{aligned} \quad (13)$$

χ is the electronegativity.

We will use only the former principles of the hardness concept such as indicated by Eqs. (11) and (12).

Then the basic principles of the method are as follows:

(i) difference in electronegativities drives the electron transfer, while the sum of hardness attenuates this; (ii) an equilibrium mean electron chemical potential can be defined for

a molecule or a crystal and then electrons have to be located inside the whole molecule (or crystal) accordingly with the electronegativities and hardnesses of the different species forming the molecule or the crystal. Practically, it is simply necessary to compute the equalization of the chemical potentials of the different charge clouds upon bond formation, and then to determine atomic charges in molecules. It is very simple for diatomic molecules A–B. For any electron transfer dN from B to A at the internuclear distance r , the change in energy is

$$\begin{aligned} dE = & \left[\left(\frac{\partial E}{\partial N_A} \right)_{N_B, r} - \left(\frac{\partial E}{\partial N_B} \right)_{N_A, r} \right] dN \\ & + \left(\frac{\partial E}{\partial r} \right)_{N_A, N_B} dr. \end{aligned} \quad (14)$$

At $r = r_e$, the internuclear equilibrium distance $dr = 0$ and there is an equalization of the effective electronegativities of A and B, ensured by a change of the effective charges. Using the above definition of the hardness, one gets

$$\chi_A = \chi_A^0 - \eta_A q_A = \chi_B^0 + \eta_B q_B = \chi_B = \bar{\chi}. \quad (15)$$

However, this calculation, which is simply a calculation of the two charges, could be complex for crystals where forces act at relatively long distances and where a summation is necessary. Two mathematical methods to achieve fairly rapid convergence have been developed by Ewald and Bertaut [39]. Only the knowledge of the solid structure is then necessary.

5. Calculation

The first step of the calculation is the building of a matrix corresponding to a summation of the electrostatic influence relative to the different locations of the species constituting the crystal. This is achieved using the crystal structure issued from Databanks and the relationships defined by the space-group of the crystal. Details of such calculations giving the Madelung constant M and the Madelung tensor M_{ij} are given elsewhere [40]. One of the results of the calculations is the electrostatic part of the lattice energy, i.e., the main attractive part of this energy, when considering ionic solids:

$$U_e = -\frac{N_a M e^2}{r_e}. \quad (16)$$

The choice of r_e , the internuclear distance, is detailed in Refs. [40,41]. It must be emphasized that this calculation of the lattice energy assumes that the crystal is fully ionic. When attributing electronegativity and hardness values to the different species, some crystals can be considered as not fully ionic and then the crystal bond energy is only partially due to the electrostatic interactions.

We have chosen, following Henry, to use the electronegativity scale due to Allen [42], which is related to spectroscopic characteristics of the atom and a hardness scale built

using the molecular diameters of the species [28]. In this model, the hardness is linked to the radius of the atom, considered as a sphere of radius r with a uniformly distributed electric charge q :

$$E(q) = \frac{e^2 q^2}{8\pi \epsilon_0 r} \quad \text{gives} \quad \chi = \left(\frac{\partial E}{\partial q} \right) = \frac{e^2 q}{4\pi \epsilon_0 r} \quad \text{and} \\ \eta = \left(\frac{\partial^2 E}{\partial q^2} \right) = \frac{e^2}{4\pi \epsilon_0 r}. \quad (17)$$

The radius is taken as the size of the diffuse orbital. This hardness scale is detailed in Ref. [28b]. Then the calculation does not depend on assumptions or relative scales but only on physical values that can be determined by spectroscopic techniques or quantic calculations. This point has to be emphasized: the calculation does not depend on adjustable parameters.

The calculations can be carried out for infinite crystals by using crystal parameters issued from Databanks. The effective electronegativity is

$$\bar{\chi} = \chi_i^0 + \frac{e}{4\pi \epsilon_0 r_i} q_i + \frac{1}{4\pi \epsilon_0} \sum_{j=1}^n M_{i,j} e q_j \quad \text{with} \\ \sum_{i=1}^n q_i = z. \quad (18)$$

One has to emphasize that the Madelung tensor $M_{i,j}$, which takes into account the geometry of the studied crystal, is one of the main terms of the calculation. The computation of the partial charges q_i is straightforward. From this distribution, it is possible to calculate a summation called by Henry the electrostatic balance (EB):

$$EB = \frac{e^2}{8Z\pi \epsilon_0} \sum_{i=1}^n \sum_{j=1}^n M_{i,j}(q, z) q_i(q, z) q_j. \quad (19)$$

If one uses the theoretical total charges instead of the partial charges in Eq. (19), this gives obviously the electrostatic part of the lattice energy, U_e , defined above. Then, EB can be considered as the effective electrostatic part of the bond energy. It must be emphasized that it is possible to go from the attractive part of the energy to the total energy, i.e., for example to take into account the repulsive part using the Born–Landé equation [41]. At first level of approximation, the electrostatic energy that takes into account the repulsive forces is about 90% of the attractive part.

In this general framework, it is possible to build models of finite layers, developed along different axes or hkl planes. It can be assumed that only long-range forces are modified when comparing infinite crystal and finite layer. Indeed, a strong modification of the electrostatic energy is observed when developing a layer. This is related to the variation of the Madelung term, as emphasized before. What is observed is the influence of the length of the crystallite on the electrostatic energy. This energy can be extrapolated to a value corresponding to a layer, infinite in two directions

of the space and finite in the other one. Assuming that the other parts of the energy (mainly due to dispersive forces) do not vary when modifying the dimension of the crystal, the difference of electrostatic energy can be considered as the total variation of the attractive energy between a semi-infinite layer and an infinite crystal. Then, it can be attributed to the attractive part of the energy of cohesion between the crystal and the considered part of the crystal, i.e., the energy required to obtain the separation,

$$H_{\text{coh}}^{\text{attr}} = [H^{\text{AB}}(\text{crystal}) - H^{\text{AB}}(\text{layer})] / A_s^c, \quad (20)$$

where A_s^c is the surface area of the considered layer.

If the considered layer is build along two crystal axes, it is easy to relate the surface area acting in the defined process to the molecular lengths, for instance to the cell lengths a , b , and c . By definition, per unit surface area, the energy of cohesion is twice the energy of surface tension.

6. Ice characteristics

The characteristics of ice have been taken from Leadbetter et al. [43]. Their structural parameters have been obtained for D₂O by profile refinement of neutron powder diffraction data. It corresponds to an hexagonal ice denoted Ih. The values of the parameters used here are the following: $a = 4.504$ Å; $b = 4.504$ Å; $c = 7.334$ Å; $\alpha = 90.0^\circ$; $\beta = 90.0^\circ$; $\gamma = 120.0^\circ$; space group: $P6_3/mmc$. The locations of the atoms are listed in Table 1. Some masks have been added in our calculation in order to take into account the relative site occupancy of hydrogens.

The resulting structure is drawn in Fig. 1, but the relative occupation of H atoms has not been reported on Fig. 1 for sake of simplicity.

7. Results

7.1. Infinite crystal

The values used in the computation, i.e., the electronegativities, hardnesses and corresponding softnesses, expressed as the length of the s -orbital are listed on Table 2. The data obtained are listed on Table 3.

The values obtained for the partial charges appear realistic, and the electronegativity of the network stands in the

Table 1
Atomic coordinates of ice Ih, to be referred to the cell dimensions given in the text (from Ref. [43])

Atom	x	y	z	Occupation
O	1/3	2/3	0.0636	100%
H1	1/3	2/3	0.1993	50%
H2	0.4532	0.9064	0.0164	50%

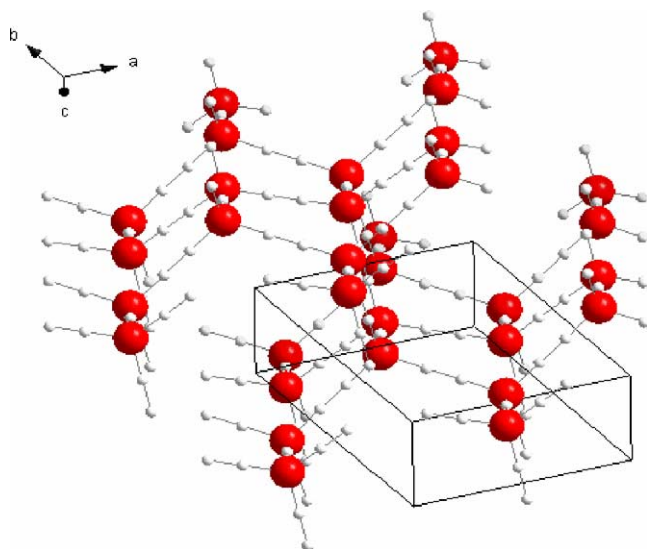


Fig. 1. The structure of ordered ice Ih, space group $P6_3/mmc$. All the hydrogens have been drawn here for sake of simplicity. The actual ice Ih and the one used in the computation correspond to a site occupancy of hydrogens of 0.5. The unit cell is drawn in full line.

Table 2

Atomic electronegativities, hardnesses, and softnesses (expressed as the size of the s -orbital) used in the computation (from Refs. [28,42])

Atom	Electronegativity (V)	Hardness (V)	Softness (pm)
O	21.36	31.9999	45
H	13.61	27.169	53

Table 3

Results obtained from the calculation for the ice Ih

Attractive electrostatic part of the lattice energy	5125 kJ/mol
Mean electronegativity of the crystal	14.85 V
Electrostatic balance (EB)	212.6 kJ/mol
Mean hardness of the crystal	8.93 V
Charge on the oxygen	-0.407
Average charge on the hydrogens	0.204

range defined by the electronegativities of the atoms composing the network. The value of 212.6 kJ/mol can be compared to the enthalpy of formation of liquid water, which is about 285.8 kJ/mol (the enthalpy of fusion of ice at 0 °C is about 6.0 kJ/mol). Moreover, assuming that the cohesive energy h_i defined above is the value admitted for an hydrogen bond (18 kJ/mol), we obtain using Eq. (8), 24 neighbors for a molecule, that seems correct. Then the values obtained are very satisfying.

7.2. Layers

We have considered here that a “layer” of water is composed of two molecules superposed along the transversal axe. It corresponds to a conservation of the cell structure along this axe (see Fig. 1). This means that we have developed the layer by multiplying the cell by a triplet, $(x, 1, x)$, for example, for the layer developed along the axes a and c ,

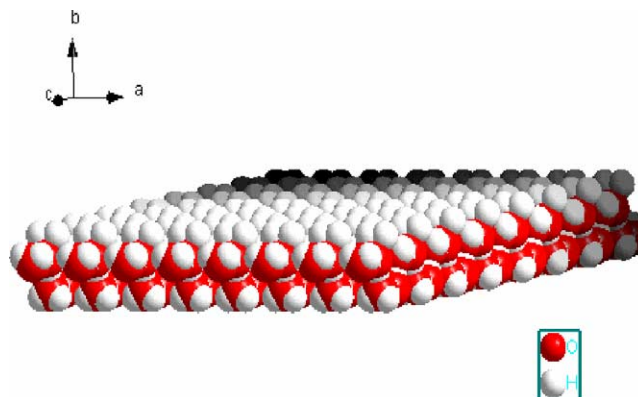


Fig. 2. Schematic picture of a layer developed along plane ac . This picture is given here to illustrate the text, but does not correspond exactly to a file used in the computation.

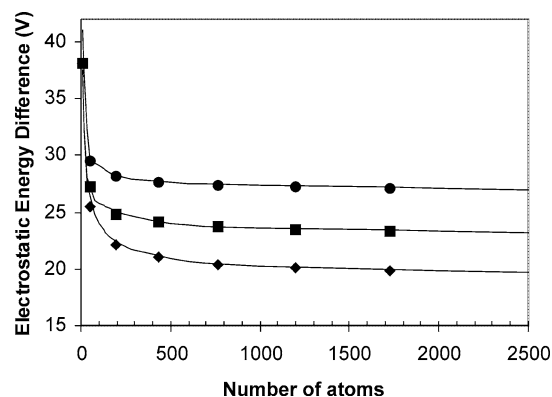


Fig. 3. Variation of the differences between the energies of the layers developed along the different axes and the energy of the infinite crystal vs the number of atoms in the layer used in the computation.

x being an entire number. Another choice, such as a triplet (x, y, x) , corresponding to a multiple along the transversal axe should give an energy variation corresponding to the break of the unit cell. This value cannot correspond to the energy of cohesion, but to the energy related to grinding, which is a more complex process. Moreover, the two parts then created could not correspond to stoichiometric crystals. It must be pointed that it is necessary to build here neutral layers, i.e., composed of H_2O molecules, and not of hydrogen or oxygen single atoms. As indicated above, the electrostatic part of the energy varies when developing a layer. We have calculated the energy for layers built along planes (a, b) , (a, c) , and (b, c) . Such a layer of 768 atoms developed along the directions (a, b) is sketched on Fig. 2.

We report on Fig. 3 the variation of the electrostatic part of the energy of the layer versus the number of molecules, for the three planes considered (the energy is reported as the difference between the energy of the layer and of the infinite crystal). The energy differences vary very slowly when building layers of more than 500 atoms. We have graphically extrapolated this value for 2500 atoms, which seems sufficient when taking into account the precision expected.

Table 4

Results obtained for three semi-infinite planes developed along *ab*, *bc*, and *ac*

Plane	<i>ab</i>	<i>bc</i>	<i>ac</i>
Extrapolated energy difference (kJ/mol)	19.8	23.2	27
Area of one face of the plane (m ² /mol)	26448.5	49726.5	49726.5
Molecular cross-sectional area (Å ²)	4.4	8.2	8.2
Surface energy (mJ/m ²)	187	117	136

The area of one molecule in the corresponding plane is also reported.

The results are reported on Table 4 for the different planes. These values have been divided by twice the area of the considered plane, considering that the perpendicular direction is negligible. The values taken for the area correspond to the cell parameters reported on Table 1. The interfacial energy obtained is also reported on Table 4.

8. Discussion

It appears in Table 4 that the surface energy obtained depends on the different directions taken when building the layers. This makes sense considering that ice is not symmetrical in the three directions of space. We will consider that we can take an average value for the sake of comparison with the water surface energy. Then, we obtain an average value of 147 mJ/m², which is very near the experimental value obtained for liquid water. Comparison of the EB obtained with the enthalpy of formation could indicate that these values are underestimated, but we can consider that the electrostatic part is the only part varying during the process of extension of the layer. However, in the electrostatic part, we have not taken into account the energy of repulsion. Then the actual surface energy of ice should be lower, about 140 mJ/m². Nevertheless, the main point is that we obtain the good order of magnitude, at a level of accuracy, which is not usual concerning the surface of solids. However, such a good result is not so surprising, because calculations based on electronegativity models give generally very good estimation of the reticular energy. Then the reticular energy computed for a layer of water must be realistic, even though this thermodynamic value does not correspond to an experiment. The only assumption of the computation we propose is to consider that the variation of energy due to the adhesion of a layer to a infinite number of layers is only due to the variation of partial charges of the atoms. This is realistic if the studied solid can be considered as composed of discrete and well-identified layers. The hydrogen bond characteristics insure such a structure for ice Ih. Then, the assumption we made has a physical sense.

9. Conclusion

The use in surface chemistry of models coming from inorganic chemistry has still shown interesting results. Concepts of hard–soft acid–base (HSAB), which are very near

to covalent–electrostatic concepts developed by Drago et al. [44], have been applied with significant results in the fields of contact angle and of catalysis. Fowkes has presented powerful calculations of the interfacial tensions using such methods. In this paper, we have used the HSAB concept, and more particularly the methods developed in order to analyze the partial charges in solid networks [45]. The model we use and the corresponding calculation does not use adjustable parameters but data issued from atomic characteristics of molecules: Allen spectroscopic electronegativity and *s*-orbital radius. This means that calculations give realistic values of the energy and not values relative to scales without dimension. This is clear when looking at the mean electronegativity obtained for ice, which stands realistically between the spectroscopic electronegativities of oxygen and hydrogen.

One of the main results of the computation is the actual electrostatic part of the attractive energy of the solid network. We have assumed that the differences in this energy observed between a semi-infinite crystal developed along two directions of the cell and the infinite crystal is related to the energy of cohesion of the layer developed. This energy of cohesion is related to the surface energy. Then we have calculated a mean surface attractive energy for the three faces of the ice Ih. The result is surprisingly good, very near of the result expected, which is supposed close to the surface energy obtained for liquid water. However, such a calculation is limited to a small number of atoms (< 2000), that is the obvious limitation of such computer chemistry. But here, this number appears sufficient, because the variation of the electrostatic energy varies slowly above 500 atoms. Such a calculation is also limited to few solid networks, which can be easily divided in neutral layers or in stoichiometrically equilibrated layers. And finally, the main limitation is the fact that, for other solids, it is quite impossible to compare these results with direct determinations. But the method appears promising and in the near future, we will apply it to clay surfaces, for which we dispose of some experimental estimations [24,46].

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