Hartman Perdok Method
for Analysis of Growth form of Crystals

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This paper deal with an analysis of the growth form of crystals from the point of view of Hartman Perdok method of analysis. We present in the present paper a parallel of three types of crystals like : betulinic acid, urea and quartz crystals that from starting Hartman Perdok method , knowing the structure of each crystal we can obtained by using simulations the growth form of these crystals. The simulations are in good agreements obtained in experiment with the crystal for quartz and urea crystals but for betulinic acid the studies are only preliminaries and need to be improved .

Keywords: crystals, growth form, Hartman Perdok method, betulinic acid, urea, quartz

Hartman and Perdok theory of Periodic Bond Chain explains crystal morphology starting from the crystal structure [1]. In the Hartman Perdok theory was introduced the PBC (Periodic Bond Chain) term, which represent an uninterrupted chain of first neighbor bonds having a periodicity of the lattice. So it can be described three types of faces: 1) F – the face which is parallel with at least two different sets of PBC; 2) S – the face which is parallel with only one PBC and 3) K – the face which is not parallel with any PBC[1]. Are taking into account intermolecular energies and is possible to predict the growth form [2]. Hartman and Bennema introduced the proportionality of the growth rate of the F face with its attachment energy [3]. In molecular crystals Coulomb energies are more important than Van der Waals energies [2].

The crystal structure determines the surface structure and the surface related energies: specific surface energy, attachment energy, and slice energy. Attachment energies are supposed to be directly proportional to the growth rates of F faces [3]. Calculations of attachment energies allow for the construction of theoretical growth forms. The theoretical growth forms can based on the Coulomb interactions energies (by using an electrostatic point charge model). For a more rigorous model can be used the contributions of van der Waals interactions and Born repulsions. Can be computed the theoretical equilibrium forms based on the specific surface energies.

In the present paper, by using Hartman and Perdok method, is presented the growth form of crystals related to the attachment energy.

These methods were applied in previous studies on quartz [4], on rutile [5] and on melilite [6] and were obtained the growth and equilibrium forms of these types of crystals.

The simplest method for predicting crystal morphology from knowledge of the crystal structure is to assume that the slowest growing and hence largest crystal faces are those with the greatest interplanar spacings, d_{hkl}, reflecting the weakest interactions between the face and next growth layer [7]. This is the basis of BFDH method, which has evolved from work by Bravais, Friedel and Donnay Harker [11,12] and is very useful in determining which crystal faces should be considered in morphological studies. The influence of the intermolecular interactions on crystal morphology was taken into account qualitatively by Hatman and Perdok [1]. F (flat) faces where the slice d_{hkl} contains at least two periodic Periodic Bond Chains (PBCs) parallel to the face which usually dominate the morphology. In contrast faces with fewer strong interaction in the layer classified as S (stepped) or K (kinked) faces which grow much faster. Hartman-Perdok theory become quantified through the calculation of attachment energies Ea. The attachment energies Ea (hkl) is defined as the energy per molecule (or building unit: BU) released on attachment of stoichiometric growth slice (a slice of crystal parallel to the growing face) to a growing (hkl) crystal surface [7,3]. The relative growth rates of faces will be proportional to the attachment energy , has been justified for F faces which grow according to a layer growth mechanism [7,3]. Molecular dynamic simulations of pure solvent [2,10,7] or saturated solutions [2] above different crystal faces have been performed to provide molecular level insight into solvent effects. Estimates of binding energy of solute and solvent to kinks and edges can provide some of the parameters required for modeling 2D nucleation or spiral growth rates [7].

To develop theories of molecular crystallization process we require a program that is capable calculating a wide range of surface properties, including surface –surface, surface –layer and surface- molecule interaction considerable flexibility in the types of molecular arrangement that can be treated [10]. To use approach to calculate attachment energies Ea for predicting morphologies of organic crystal were used programs such HABIT [11,12] or CERIUS [7] is from slice and crystal energies calculating by dividing the summation of the intermolecular interactions within the perfect infinite crystal. An alternative approach as to calculate it from the definition using 2D periodic boundary condition as implemented in the MARVIN program [7] HABIT is limited to isotropic atom-atom potentials and use point charges on atoms plus inter-atomic Lennard-Jones or Buckingham functions [12,7]. Simple interaction potentials can be successfully, is well establish that it is necessary to go beyond the atomic point charge model to reproduce the structure of many van der Waals complexes and organic crystal structures [13,7]. The distributed multipole analysis (DMA) method use a higher order for electrostatic

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moments [14,7]. Model of potential using DMA electrostatic models and empirical repulsion-dispersion models have been applied to study the interaction of a wide range of organic molecules in the gas and crystalline phase [15,18] Engkvist et al. used such models for crystallization of urea [10] by using ORIENT program package to study the morphology of crystalline urea . Based on these results we obtained in the present paper the growth form of urea crystals, to continue the results of Engkvist [31]. Engkvist conclude that polar facets of urea crystals cannot be predicted by attachments energy model.

Singh & Banerjee described the computational details to calculate lattice energy as Molecular Attachment Energy (MAE) and Molecular Detachment Energy (MDE) for urea molecule s of different orientations [19]. For this purpose they used CRYSTAL09 program in order to calculate the effect of dispersive interactions density functional theory based on calculations with empirical dispersion terms. Civalleri et al. used a method where the structure and the lattice energies of molecular crystals give a model for the crystal which is in a good agreement with experimental results [17,18]. Singh and Banerjee used a special method to obtain structure and various energetic characteristics of growth and dissolutions of different faces of urea crystals [19]. The symmetry of slices is maintained during all surface relaxation calculations. In CRYSTAL09 code optimization convergence is checked on the root mean square and the absolute value of the largest component of both the gradient and the estimated displacements.

Matsui developed for both crystals and melts the CMAS system of the transferable potential model [9]. The CMAS model is used in molecular dynamic simulations to reproduce structural data, lattice parameters, bulk module, and both average and individual 27 oxides and silicates. This model reproduces in a reliable way the bulk module and the inter-atomic distances. The Matsui coefficients are used to calculate the short-range of the applied energy to determine the growth form of crystals for different situations of the reduced charges models.

Woensdregt use in his work as us a model calculations in an electrostatic point charge that have been performed. In this model the computations are relatively simple because are used the Madelung formulas. The limitations in this model is the ionic character , although the influence of the partly covalent character of certain ionic bonds such as Si-O and Al-O bonds can be estimated from calculations whit adjusted electric charges [21].

Structure of urea crystals

The structure for urea crystals ($CO(NH_2)_2$) having space group P -42$_1$m and the parameters for the unit cell : a=b= 5.5780 Å and c = 4.6860 Å [24¸31] is presented in table 1.

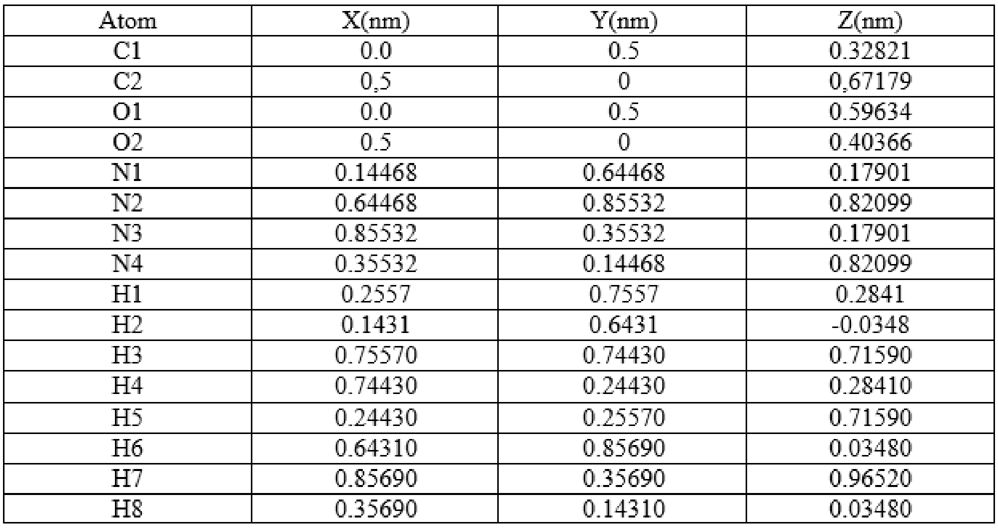
Theoretical growth and equilibrium forms of urea crystals ($CO(NH_2)_2$) were constructed from the calculated attachment energies see [31] which are assumed to be directly proportional to the growth rate for F faces. Crystal structure determines the surface structure and related surface energies, e.g. specific surface energy, attachment energy, dispersion because Van der Waals attraction and Born repulsions. Were obtained this energies for urea crystals ($CO(NH_2)_2$) as they control the crystal growth form and the equilibrium form of a crystal [31].

Structure of quartz crystals

Were used coordinates as determined by Glinnemann et al. [23]. The used Space Group symmetry was P3$_1$2$_1$ with a hexagonal unit cell constants a = b = 4.921 Å and c = 5.163 Å as in table 2.

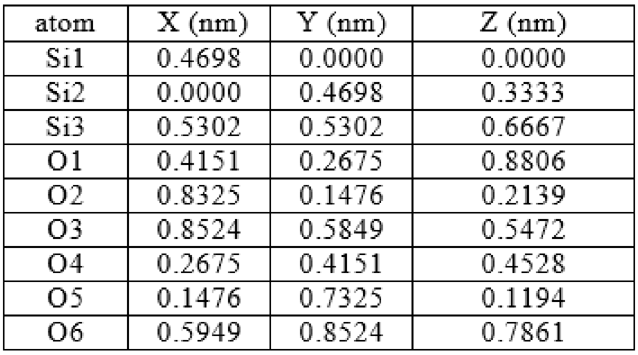
Structure of betulinic acid crystals

For betulinic acid was used the next structure: space group Space Group: P2$_1$2$_1$2$_1$ orthorhombic system of crystallization and the parameter of the unit cell a= 7.0988Å b= 12.3864Å c= 33.2745Å [30] as in table 3.



Atom	X(nm)	Y(nm)	Z(nm)
C1	0.0	0.5	0.32821
C2	0,5	0	0,67179
O1	0.0	0.5	0.59634
O2	0.5	0	0.40366
N1	0.14468	0.64468	0.17901
N2	0.64468	0.85532	0.82099
N3	0.85532	0.35532	0.17901
N4	0.35532	0.14468	0.82099
H1	0.2557	0.7557	0.2841
H2	0.1431	0.6431	-0.0348
H3	0.75570	0.74430	0.71590
H4	0.74430	0.24430	0.28410
H5	0.24430	0.25570	0.71590
H6	0.64310	0.85690	0.03480
H7	0.85690	0.35690	0.96520
H8	0.35690	0.14310	0.03480

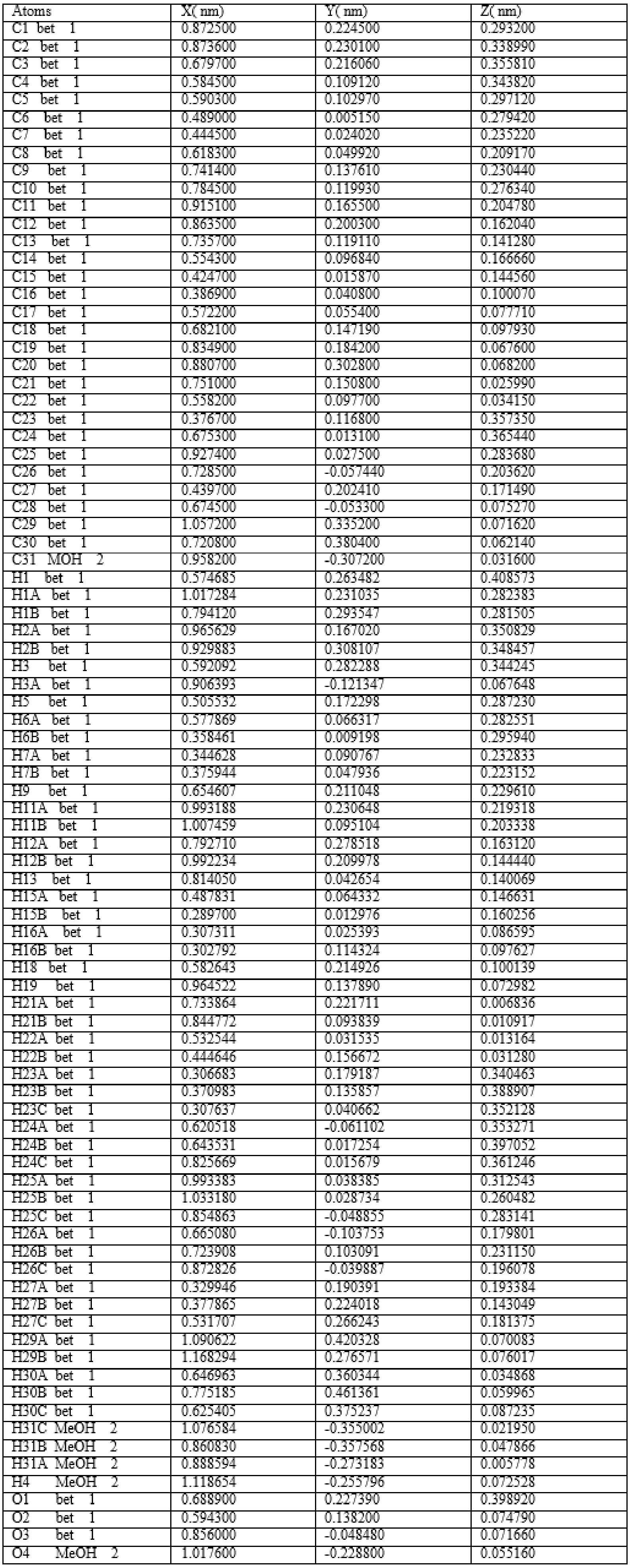
Table 1
COORDINATES FOR UREA [31]



atom	X (nm)	Y (nm)	Z (nm)
Si1	0.4698	0.0000	0.0000
Si2	0.0000	0.4698	0.3333
Si3	0.5302	0.5302	0.6667
O1	0.4151	0.2675	0.8806
O2	0.8325	0.1476	0.2139
O3	0.8524	0.5849	0.5472
O4	0.2675	0.4151	0.4528
O5	0.1476	0.7325	0.1194
O6	0.5949	0.8524	0.7861

Table 2
COORDINATES FOR SiO_2 [23]

Table 3
STRUCTURE OF BETULINIC ACID + MeOH (METHANOL)[30]



Atoms	X(nm)	Y(nm)	Z(nm)
C1 bet 1	0.872500	0.224500	0.293200
C2 bet 1	0.873600	0.230100	0.338990
C3 bet 1	0.679700	0.216060	0.355810
C4 bet 1	0.584500	0.109120	0.343820
C5 bet 1	0.590300	0.102970	0.297120
C6 bet 1	0.489000	0.005150	0.279420
C7 bet 1	0.444500	0.024020	0.235220
C8 bet 1	0.618300	0.049920	0.209170
C9 bet 1	0.741400	0.137610	0.230440
C10 bet 1	0.784500	0.119930	0.276340
C11 bet 1	0.915100	0.165500	0.204780
C12 bet 1	0.863500	0.200300	0.162040
C13 bet 1	0.735700	0.119110	0.141280
C14 bet 1	0.554300	0.096840	0.166660
C15 bet 1	0.424700	0.015870	0.144560
C16 bet 1	0.386900	0.040800	0.100070
C17 bet 1	0.572200	0.055400	0.077710
C18 bet 1	0.682100	0.147190	0.097930
C19 bet 1	0.834900	0.184200	0.067600
C20 bet 1	0.880700	0.302800	0.068200
C21 bet 1	0.751000	0.150800	0.025990
C22 bet 1	0.558200	0.097700	0.034150
C23 bet 1	0.376700	0.116800	0.357350
C24 bet 1	0.675300	0.013100	0.365440
C25 bet 1	0.927400	0.027500	0.283680
C26 bet 1	0.728500	-0.057440	0.203620
C27 bet 1	0.439700	0.202410	0.171490
C28 bet 1	0.674500	-0.053300	0.075270
C29 bet 1	1.057200	0.335200	0.071620
C30 bet 1	0.720800	0.380400	0.062140
C31 MOH 2	0.958200	-0.307200	0.031600
H1 bet 1	0.574685	0.263482	0.408573
H1A bet 1	1.017284	0.231035	0.282383
H1B bet 1	0.794120	0.293547	0.281505
H2A bet 1	0.965629	0.167020	0.350829
H2B bet 1	0.929883	0.308107	0.348457
H3 bet 1	0.592092	0.282288	0.344245
H3A bet 1	0.906393	-0.121347	0.067648
H5 bet 1	0.505532	0.172298	0.287230
H6A bet 1	0.577869	0.066317	0.282551
H6B bet 1	0.358461	0.009198	0.295940
H7A bet 1	0.344628	0.090767	0.232833
H7B bet 1	0.375944	0.047936	0.223152
H9 bet 1	0.654607	0.211048	0.229610
H11A bet 1	0.993188	0.230648	0.219318
H11B bet 1	1.007459	0.095104	0.203338
H12A bet 1	0.792710	0.278518	0.163120
H12B bet 1	0.992234	0.209978	0.144440
H13 bet 1	0.814050	0.042654	0.140069
H15A bet 1	0.487831	0.064332	0.146631
H15B bet 1	0.289700	0.012976	0.160256
H16A bet 1	0.307311	0.025393	0.086595
H16B bet 1	0.302792	0.114324	0.097627
H18 bet 1	0.582643	0.214926	0.100139
H19 bet 1	0.964522	0.137890	0.072982
H21A bet 1	0.733864	0.221711	0.006836
H21B bet 1	0.844772	0.093839	0.010917
H22A bet 1	0.532544	0.031535	0.013164
H22B bet 1	0.444646	0.156672	0.031280
H23A bet 1	0.306683	0.179187	0.340463
H23B bet 1	0.370983	0.135857	0.388907
H23C bet 1	0.307637	0.040662	0.352128
H24A bet 1	0.620518	-0.061102	0.353271
H24B bet 1	0.643531	0.017254	0.397052
H24C bet 1	0.825669	0.015679	0.361246
H25A bet 1	0.993383	0.038385	0.312543
H25B bet 1	1.033180	0.028734	0.260482
H25C bet 1	0.854863	-0.048855	0.283141
H26A bet 1	0.665080	-0.103753	0.179801
H26B bet 1	0.723908	0.103091	0.231150
H26C bet 1	0.872826	-0.039887	0.196078
H27A bet 1	0.329946	0.190391	0.193384
H27B bet 1	0.377865	0.224018	0.143049
H27C bet 1	0.531707	0.266243	0.181375
H29A bet 1	1.090622	0.420328	0.070083
H29B bet 1	1.168294	0.276571	0.076017
H30A bet 1	0.646963	0.360344	0.034868
H30B bet 1	0.775185	0.461361	0.059965
H30C bet 1	0.625405	0.375237	0.087235
H31C MeOH 2	1.076584	-0.355002	0.021950
H31B MeOH 2	0.860830	-0.357568	0.047866
H31A MeOH 2	0.888594	-0.273183	0.005778
H4 MeOH 2	1.118654	-0.255796	0.072528
O1 bet 1	0.688900	0.227390	0.398920
O2 bet 1	0.594300	0.138200	0.074790
O3 bet 1	0.856000	-0.048480	0.071660
O4 MeOH 2	1.017600	-0.228800	0.055160

Energy Calculations

The attachment energy, E_a is the energy released per mole when a new slide of a thickness d_{hkl} crystallizes on an already existing crystal face (hkl) [7]. The slice is, in the case of an F face, the elementary growth layer. Its thickness d_{hkl} is equal to the period with which the same surface configuration is repeated. This interplanar spacing d_{hkl} is determined by the same extinction conditions as X-ray reflections. The attachment energy is the sum of all the interaction energies over all the ions that belong to one crystallizing unit and over all slices d_{hkl} where the crystal has been divided parallel to the crystal face (hkl).

The surface related energies were calculated using a point charge model [21] . The selected force field equations calculations take into consideration only the Coulomb interactions. Recently, the contributions by the van der Waals interaction energies and Born energies can also be computed [5,6]. Since decreasing the effective point charge can compensate for the partly covalent character of the ionic bond, the energy calculations in a point charge model with lower effective charges may be more reliable.

An approximation of the potential energy using CMAS model is [22]:

$$E_{acor} = -E_a - E_{vdW} + E_B \quad (1)$$

where the terms in the sum are:

$$E_{acor} = -\frac{q_i q_j}{r_{ij}} - \frac{C_i C_j}{r_{ij}^6} + f\left(B_i + B_j\right) e^{\left[\frac{\left(A_i + A_j - r_{ij}\right)}{\left(B_i + B_j\right)}\right]} \quad (2)$$

In both eqs. (1) and (2) the first term E_a is the attachment energy (when only Coulomb interactions are taken into account), the second term E_{vdw} is the energy when only van der Waals interactions are taken into account, while the last term E_B , is the interaction energy when only Born repulsions are taken into account, where f = 4.184 kJ mol^{-1}. A_i and B_i are the repulsive radii and softness parameters of the ion i, r_{ij} is the interatomic distance between atoms i and j, respectively, and q_i is the net charge.

The specific surface energy is [20]:

$$\gamma = \frac{f Z_p d_{hkl} \sum_{m=1}^{\infty} m E_m}{2 V_p}, \quad (3)$$

where f=-166.036 is a conversion factor to obtain the surface in the unit of mJ·m^{-2} instead of kJ ·mol^{-1}, Z_p is the number of the molecules in the primitive unit cell with volume V_p, and E_m is the partial attachment energy of slice m with the interplanar spacing d_{hkl} (- when we take into account partial attachment energies because of ecranations - this is the motivation of using fractional charges in the system.

Results and discussions

Energies calculations using Hartman Perdok Method

Using Hartman Perdok Method we can calculate attachment energies (Ea) for simulations and predictions of F faces .

That was done for urea crystals [31] and were found energies in the range of 94.7 kcal/mol for the face 001 and 167.54 kcal/mol for the face -1-1-1. A bigger face seems to be 110 with an energy of 60.80 kcal/mol.

For the quartz crystals were done the same calculations and the results were like 249,175 kcal/mol for the face 10-10, 305.74 kcal/mol for the smallest face 01-11 and 277.697 kcal/mol for the face 10-11.

For betulinic acide were done only the preliminaries analysis and at the beginning we get 0.2840 kcal/mol.

Growth form of crystals

In figures 1 a,b,c and 3 a we can see the growth form of the studied crystals .

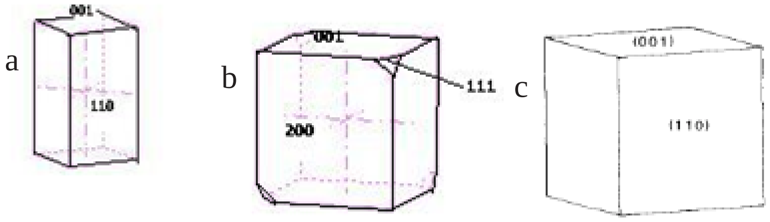


Fig. 1a, b. urea crystals obtained from simulations [31] and
c urea crystals obtained from simulations by from Boeck et al [2]

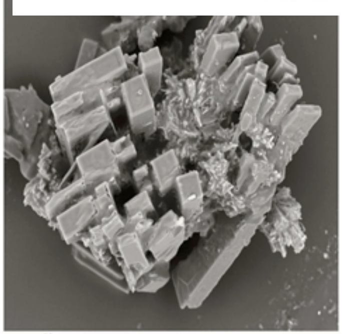


Fig. 2. urea crystals obtained in the lab [32]

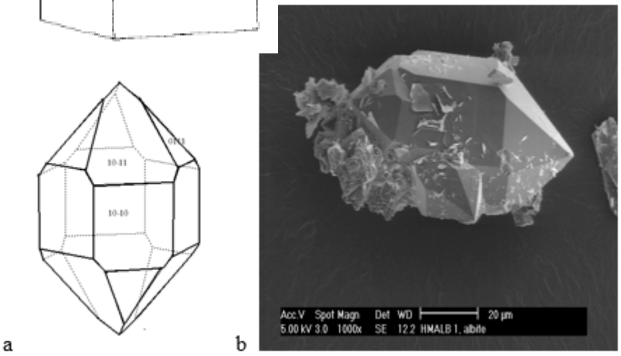


Fig. 3a. Quartz crystals obtained in simulations [5],
b. quartz crystals obtained in the experiment

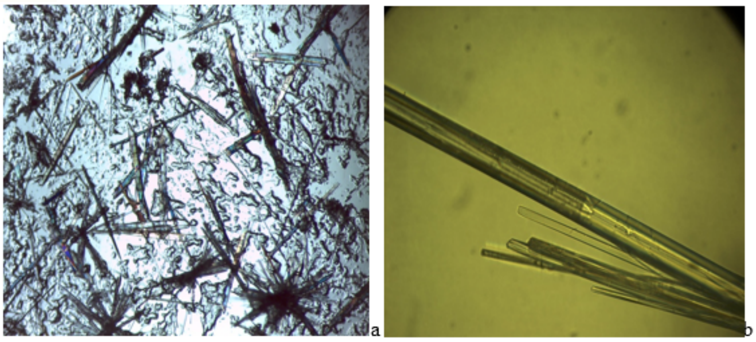


Fig. 4a, b. Betulinic acid crystals obtained in the experiment

In figure 1 a , b we can see the growth forms obtained in simulations for urea crystals [31]. We can observe that these are in good agreement with literature which similar to that obtain by Boek et al. [2] from figure 1 c.

Figure 3 a is a growth form of a quartz crystal as in [5].

We can observe that figures 1 a,b,c and figure 3 a are in good agreement with those obtained from simulations. Figure 4 is a very good proof that betulinic acid can be obtained in the laboratory but in this moment with no proof from simulations. This is a good work for the future research.

Hartman Perdok theory can not explain the asymmetric growth of the opposite polar faces because it is based on the fact that facet growth occurs due to the adsorption of slice of thickness of the order of d_{hkl} on the existing surface. In order to compare the results for the lattice energy with corresponding data which are related to the enthalpy of sublimation ΔH_{sub}. From the experimental data on enthalpy the lattice energy E_{latt} at 0K can be obtained as : $E_{latt} = -\Delta H_{sub} - 2RT$, where R and T are gas constant and temperature at which enthalpy of sublimation has been measured, 2RT is the enthalpy correction term. Singh used in his work results of MAE for two types of molecules having (111) and (-1-1-1) faces of urea crystals [19].

Conclusions

In the present paper, by using Hartman and Perdok method, is presented the growth form of crystals related to the attachment energy. A transferable potential model was used in an molecular-dynamics simulations to reproduce structural data, lattice parameters, bulk moduli and interatomic distances. Because of the reliability of this model to reproduce bulk moduli and interatomic distances we have used the coefficients in order to calculate the short range contributions to the attachment energy.

Attachment energy have to be directly proportional for F faces to their growth rates .

Model for calculations is an electrostatic point charge model. This model was used for different types of crystals: like quartz and urea with good results . But for betulinic acide the number of atoms in the structure is too big and needs further development of programs or improuvements of the present programs to proofs the experimentals for obtaining of betulinic acid. We consider in the present paper that by using Hartman and Perdok method is not enough to predict and calculate attachment energies and then growth form of crystals with more then 50 atoms in the structure.

This paper deal with an analysis of the growth form of crystals from the point of view of Hartman Perdok method of analysis. Hartman and Perdok theory of Periodic Bond Chain explains crystal morphology starting from the crystal structure. We presented in the present paper a parallel of three types of crystals like : betulinic acid, urea and quartz crystals that from starting Hartman Perdok method , knowing the structure of each crystal we can obtained by using simulations the growth form of these crystals. The simulations are in good agreement for quartz and urea crystals by for betulinic acid the studies are only preliminaries and need to be improved.

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References

1.HARTMAN P., PERDOK W. G., Acta Crystallogr., 8, 1955, 49.

2.BOEK E.S., BRIELS W.J., ERDEN J.VAN, FEIL D., J.Chem.Phys. 96, 1992,7010.

3.HARTMAN P., BENEMA P., J.Cryst. Growth, 49, 1980, 145.

4.NICOLOV M. F., WOEN.SDREGT C. F., J.Appl. Cryst., 35, 2002, 491.

5.NICOLOV M. F., WOENSDREGT C. F., Cryst. Res. Technol. 38, 2003, 133.

6.NICOLOV M.F., Z. Kristallogr., 219, 2004. 630.

7.O. ENGKVIST, S.L. PRICE, A.J.STONE, Phys.Chem.Chem.Phys., 2000, 2, 3017.

8.A. BRAVAIS, J. Ecole Polytech. Paris, 19, 1850, 1.

9.DONNAY J. D. H., HARKER D., Am. Minerol., 22, 1937, 446.

10. HUSSAIN M., ANWAR J., J.AM.Chem.Soc., 121, 1999, 8583.

11. CLYDESDALE G.,.DOCHERTY R. R, ROBERTS K.J., Computer Phys. Commun., 64, 1991, 311

12. CLYDESDALE G.,.DOCHERTY R. R, ROBERTS K.J., Journal of Crystal Growth, 166, 1996, 78.

13. COOMBES D.S:, PRICE S.L., WILLOCK D.J., LESLIE M., J.Phys. Chem, 100, 1996, 7352.

14. STONE A.J., Chem.Phys.Lett, 83,1981,233

15. PRICE S.L., J.Chem.Soc.Faraday Trans., 92,1996,2997

16. PRICE S.L., Rev.Comput.Chem., 14, 2000, 225.

17. CIVALLERI B., DOLL K., ZICOVICH-WILSON C.M., ,J.Phys.Chem., B111, 2007,26.

18. CIVALLERI B., C.M.ZICOVICH-WILSON, L.VALENZANO, P.UGLIENGO, CrystEngComm , 80,2008,405.

19. SINGH M. K., BANERJEE A, CrystEngComm, 15, 2013, 4143.

20. HARTMAN P., On the Crystal Habit of Fluorite. In Aleksiev El., Mincheva –Stepanova J., Padonova Tg (Eds.) Mineral Genesis. Bulgarian Acad.Sci., (1974),111-116.

21. WOENSDREGT C.F., Phys.Chem.Minerals, 19, 1992, 52.

22. MATSUI M., Phys.Chem.Minerals, 23, 1996,345.

23. GLINNEMANN J., KING H.E.JR., SCHULTZ H., HAHN TH., LA PLACA S.J., DACOL F. , Z.Kristallogr., 198, 1992, p.177 .

24. CARON, A, DONOHUE, J., Acta Cryst. 17, 1964, 544.

25. CARON, A. , DONOHUE, J. Acta Cryst. 825, 1969, 404.

26. SWAMINATHAN B., CRAVEN B.M., MCMULLAN R.K., Acta Cryst, B40, 1984, 300.

27. PRYOR, A, SANGER, P. L. Acta Cryst. A26, 1970, 543.

28. GUTH, H., HEGER, G., KLEIN, S., TREUTMANN,W. SCHERINGER,C., Z. Kristallogr. 153, 1980, 237.

29.WEI TANG, NENG-HUA CHEN, GUO-QIANG LI, GUO-CAI WANG AND YAO-LAN LI, Acta Cryst. 2014, E70, o1242–o1243

30.BORYCZKA S. BEBENEK E., JASTRZEBSKA M., KUSZ L., ZUBKO M., Kristallogr. 227, 2012, 379.

31. NICOLOV M, SZABADAI Z, TRANDAFIRESCU C, DRAGOS D, Rev. Chim.(Bucharest), **66**, no. 5, 2015, 681.

32.*** www.Dakotamatrix.Com (accessed in 07.05.2015)

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