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# New estimates of the free energy of calcite/water interfaces for evaluating the equilibrium shape and nucleation mechanisms

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## Abstract

This paper deals with several properties of calcite crystals. First, the solvated surface energies at 0K of the $\{10\bar{1}4\}$, $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, $\{01\bar{1}8\}$, $\{01\bar{1}2\}$, $\{0001\}$ and $\{21\bar{3}4\}$forms were determined by means of the COSMIC method. We find that the presence of water reduces by ~7-14% the dry surface energy at 0K, in a homogeneous way. The solvated and dry equilibrium shapes at 0K result to be nearly homothetic: in both cases the $\{10\bar{1}4\}$, $\{10\bar{1}0\}$, $\{01\bar{1}2\}$ and $\{0001\}$ forms are present.

In a second part of the paper, the free energy at 300K of the most widely studied $\{10\bar{1}4\}$/water interface has been determined ($\gamma^{300K}_{(10\bar{1}4)/w}$ = 0.412 ± 0.020 J/m$^2$) by combining simple thermodynamic relations and contact angle measurements. Some considerations on the free energy of other interfaces:$\{10\bar{1}0\}$, $\{11\bar{2}0\}\{01\bar{1}8\}$, $\{01\bar{1}2\}$, $\{0001\}$ and $\{21\bar{3}4\}$ are also proposed. We show that our results are consistent with thermodynamic constraints and fits quite well the known dependence of the solubility of calcite on grain size experimentally determined.

Furthermore, as a side result and for the first time, on the basis of on our estimate of $\gamma^{300K}_{(10\bar{1}4)/w}$ and calculated $(10\bar{1}4)$ solvated surface energy, the latter affected by the limits of the COSMIC method, a rough estimate of the vibrational energy and entropy ($\gamma^{300K,vib}_{(10\bar{1}4)/w}$), and configurational entropy ($\gamma^{300K,config}_{(10\bar{1}4)/w}$) of the $(10\bar{1}4)$/water interface is obtained: $\left(\gamma^{300K,vib}_{(10\bar{1}4)/w} + \gamma^{300K,config}_{(10\bar{1}4)/w}\right)$ = -0.066 ± 0.038 J/m$^2$.

Finally, by applying the classical nucleation theory and our estimate of $\gamma^{300K}_{(10\bar{1}4)/w}$ we calculated the activation energy for homogeneous and heterogeneous nucleation at room temperature. We found extremely high values for such thermodynamical quantity, suggesting that the direct formation of calcite should be prevented. This strongly supports the view that calcite formation should proceed throughout the early formation of an amorphous calcium carbonate phase (ACC).

## 1. Introduction

The determination of the equilibrium shape (ES hereinafter) of a crystal grown in aqueous solution requires the knowledge of the free energy of the crystal/water interfaces at the temperature of interest. It is extremely difficult to calculate such thermodynamic quantity, as it can be inferred considering that there is not a conclusive answer on calcite ($CaCO_3$) ES in aqueous systems[1-11] notwithstanding the large number of experimental and theoretical works on such crystal. Indeed, on the one hand, the estimation of the interfacial energies by *ab initio* molecular dynamic simulations of the calcite/water system are too much expensive (from a computational point of view) to be carried out; on the other hand, thermodynamical quantities calculated by means of *empirical* molecular dynamic simulations are strongly dependent upon the force fields used to describe the calcite/calcite, water/water and calcite/water interactions. As a matter of fact, although several force-fields to study $CaCO_3$ both in anhydrous and aqueous ambient have been developed in the last few decades,[7,12-17] as outlined by Raitieri et al.,[18] the majority of all of the previous studies has been focused on the accurate description of the bulk solid-state properties of calcite, with particular emphasis on its structure. Only recently the importance of thermodynamics has been stressed (i.e., free energy of the phase transitions of $CaCO_3$, free energy of the adsorption of ions) when developing a new force-field.[18,19,20] These recent force fields were used to reproduce the structure of the adsorbed water at the $\{10\bar{1}4\}$ interface, and not to determine the interfacial energy of calcite/water. Therefore, to the best of our knowledge, no reliable estimates at molecular dynamical level of the calcite/water free interfacial energies exist.

To fill such gap, in this work we aim at obtaining a physically grounded estimate of the free energy of the most widely studied $\{10\bar{1}4\}$/water interface, at room temperature ($T$ = 300K). We also point out that the free energies of the calcite/water interfaces should be very close to those between calcite and its saturated (or supersaturated) aqueous solution, due to the very low solubility of calcite in water in the usual ranges of pH and temperatures ($1.4\times10^{-2}$ g/l in water at 298 K). In order to evaluate such fundamental thermodynamical quantity, we combined simple thermodynamic relations and contact angle measurements. Some considerations on the free energy of other *strategic* interfaces, such as: $\{10\bar{1}0\}$, $\{11\bar{2}0\}\{01\bar{1}8\}$, $\{01\bar{1}2\}$, $\{0001\}$ and $\{21\bar{3}4\}$, are also proposed.

The paper is structured as follows:

(i) Firstly, in order to determine the solvated surface energies at 0K of the $\{10\bar{1}4\}$, $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, $\{01\bar{1}8\}$, $\{01\bar{1}2\}$, $\{0001\}$ and $\{21\bar{3}4\}$ calcite forms, the COSMIC method is applied. Then, the solvated ES is drawn and compared to the dry one; a comparison with the previous dry and solvated ES calculated at 0K is also performed. Furthermore, the surface structure modifications due to the presence of water is discussed. It is important to stress that these are preliminary calculations, and that we are conscious that more advanced calculations (i.e., quantum-mechanical ones) are necessary and welcome. For such a reason, in order to estimate how our results are affected by the COSMIC parameters, we tested the algorithm by using different computational parameters. We will show that different choices of the COSMIC parameters do not affect significantly the surface structures and the ES at 0K of calcite. Furthermore, it is important to underline that our estimate of the free energy at 300 K of the $(10\bar{1}4)$/water interface is independent on the calculations performed with the

COSMIC method and, as a consequence, it is not affected by the uncertainties due to the choice of the COSMIC parameters.

(ii) Secondly, the temperature effect on the solvated surface energy is evaluated. In particular, by measuring the calcite/solution contact angle on the $(10\bar{1}4)$ face and by considering the previous precise calculations of its *ab initio* dry surface energy at 0K, we estimate the free energy of the $(10\bar{1}4)$/water interface at 300K. We then discuss literature data concerning this quantity and, in the light of our results, we set forth some doubts on their validity.

(iii) Furthermore, for the first time a rough estimate of the vibrational and configurational entropy of the $(10\bar{1}4)$/water interface is obtained, by combining our estimate of the free energy of the $(10\bar{1}4)$/water interface at 300K and the solvated surface energy at 0K of the $(10\bar{1}4)$ face calculated with the COSMIC approach.

(iv) Finally, by applying the classical nucleation theory and using our estimate of the free energy of the $(10\bar{1}4)$/water interface at 300K, we estimated the thermodynamic of both the either homogeneous and heterogeneous nucleation barrier of calcite in aqueous solution.

In principle, the analysis, which is performed in this paper on calcite, is valid and applicable to every crystalline phase. We focused our attention on calcite because it occurs naturally in the structures of many organism. This wide occurrence in nature has led calcite to be one of the most extensively studied minerals in the field of biomineralization (e.g., Meldrum and Cölfen[21]). In particular, nucleation mechanisms and morphological control of calcite is potentially a topic of enormous interest and, as such, many efforts must be spent to increase our knowledge on it. Indeed, recent investigations of the mechanisms acting in biological calcification have shown that calcium carbonate crystallization frequently occurs via an amorphous and hydrated precursor rather than by direct ion-by-ion growth.[22-25] It has been established that formation of amorphous calcium carbonate (ACC) and its subsequent transformation into crystalline phases provides a competing pathway to the direct formation of the calcium carbonate polymorphs (calcite, aragonite and vaterite), with respect to the classical nucleation theory in which an activation barrier must be overcome to get a stable nucleus.[26-29] However, very recently Hu et al.[30] found that “amorphous particles formed prior to or during crystal nucleation do not grow and are not observed to act as precursors to the crystalline phase during experiments of calcite growth on organic template”. Instead, they found that calcite nucleates in an independent way and that their observations are correctly described by the classical heterogeneous nucleation. Nevertheless, in spite of that, they argued that it is not possible to exclude a non-classical formation mechanism to explain their experiments.[30] It is therefore evident that different nucleation mechanisms in aqueous solution can be hypothesized for calcite and, in order to foresee the most probable one, the calcite/water free interface energy (entering into the equations of the classical nucleation theory for determining the activation energy of the process) must be evaluated for the different crystal faces. To this end, a correct evaluation of the calcite/water interface free energy is fundamental to give a reasonable estimate of the occurrence probability of both homogeneous and heterogeneous classical nucleation with respect to the non-classical one.

## 2. Computational details

Calculations (optimizations of slab geometries and solvated surface energy estimates at $T$ = 0K) were performed by using the inter-atomic potential for calcite developed by Rohl et al.[12] (Rohl potential hereinafter) and the COSMIC model[31] implemented in the version 4.0 of the General Utility Lattice Program (GULP) simulation code[32] which, being based on force field methods, allows the calculation of structures and properties of minerals from a given set of empirical potentials.

The parameters of the Rohl potential were obtained by fitting structural data for both calcite and aragonite, as well as physical properties (elastic and dielectric constants) and phonon frequencies. This force field very successfully reproduced the equilibrium geometries and the dry surface energy values at $T$ = 0K of the $\{10\bar{1}4\}$ and $\{01\bar{1}2\}$ faces obtained from *ab initio* calculations at DFT (Density Functional Theory; B3LYP[33] and PBE[34] Hamiltonians) level,[35-37] as well as the experimental observations of the surface relaxation of the $\{10\bar{1}4\}$ form.[12] Furthermore, a fairly good agreement exists between the twinning energies of the four twin laws of calcite calculated with the Rohl potential[38] and those determined at DFT level.[39]

However, it is important to stress that more recent calcite force fields[18-20] were developed. But, at variance with the Rohl potential, they were designed to reproduce the thermodynamics of the aqueous calcium carbonate system within molecular dynamics simulations and not to reproduce the properties of the crystal surfaces. Also for this reason our calculations were performed with the Rohl potential.

The COSMIC model, which allows the calculation of the solvation energy at $T$ = 0K of a 2D periodic system like a surface, is an extension of the well-established COSMO solvation model.[40] The calculations were performed by considering the solvent water having a dielectric constant equal to 78.4. The water radius ($R_{solv}$) was set to 1.4 Å and the radius shift of water ($\delta^{SC}$) was set equal to the water radius ($\delta^{SC} = R_{solv}$), as it is usually done.[31,40] The required van der Waals radius of Ca, C and O were set to the standard values of 2.75, 1.70 and 1.52 Å, respectively.[41] The number of points per atom for the basic sphere used to construct the solvent-accessible surface (SAS) was set to 974, whereas the number of segments per atom for the SAS was set to 110. A smoothing range of 0.1 Å was used to ensure a continuous behavior of the energy surface. In order to estimate how our results are affected by the COSMIC parameters, the calculations were also performed by considering (i) $\delta^{SC} = R_{solv} = 1$ Å, (ii) the default van der Waals radii implemented in GULP (2.75, 1.53 and 1.36 Å for Ca, C and O, respectively) and (iii) the van der Waals radius of Ca equals to 2.60 or 2.90 Å.

## 2.1. Slab geometry optimization

The $\{10\bar{1}4\}$, $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, $\{01\bar{1}8\}$, $\{01\bar{1}2\}$, $\{0001\}$ and $\{21\bar{3}4\}$ surfaces were studied by using the 2D-slab model.[42] Slabs of various thickness were generated by cutting the bulk structure along the plane of interest, and eliminating the atoms in excess (surface reconstruction) in the case of the $\{01\bar{1}2\}$ and $\{0001\}$ faces, in order to cancel out the dipole moment perpendicular to the corresponding planes. These reconstructions were obtained by using a (2×2) cell for the $01\bar{1}2$ and

0001 planes, respectively, whereas the calculations on the other faces were performed by considering the (1×1) cell; for details about the surface reconstruction methods to find the most stable termination of the $\{01\bar{1}2\}$ and $\{0001\}$ faces, see the papers by Bruno et al.[36,37]

The geometry optimization was performed by considering the slab subdivided into two regions: region 1, which contains both the surface and the underlying atomic layers that are allowed to relax, and region 2 which has the same number of layers of the region 1, and contains the rest of the slab material where no relaxation with respect to the bulk crystal structure is assumed to occur.

The geometry optimization (atomic coordinates) was carried by means of the Newton-Raphson method.

Geometry optimization is considered converged when the gradient tolerance and the function tolerance (*gtol* and *ftol* adimensional parameters in GULP) are smaller than 0.0001 and 0.00001, respectively. The calculations were done by considering slabs with thickness up to 10 layers (in both the regions 1 and 2), which are sufficient to reproduce bulk-like properties at the centre of the slab and to obtain an accurate description of the surface.

## 2.2. Calculation of the solvated surface energy at 0K

According to the standard two-regions strategy employed by GULP, the specific surface energy at $T$ = 0K ($\gamma^{0K}_{CF/w}$, J/m$^2$) of a crystal face ($CF$) was evaluated from the energy of the surface block ($U_s$, region 1), by considering the contribution of the solvation energy as well (due to the presence of water, $w$), and the energy of a portion of bulk crystal ($U_b$) containing the same number of atoms as the surface block. Both energies have been referred to $A$, the common surface area of the primitive unit cell chosen:[43]

$$\gamma^{0K}_{CF/w} = \frac{U_s - U_b}{A} \qquad (1)$$

As in the COSMIC approach the configurational and vibrational entropies are not taken into account, this results to be the athermal component of the energy, usually and in the following designated *solvated surface energy at 0K*.

A ten layers slab (in both the regions 1 and 2) was sufficient to reach convergence on the surface energy value.

## 3. Results and discussion

### 3.1. The structure of the solvated surfaces at 0K

The structures of the $\{10\bar{1}4\}$, $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, $\{01\bar{1}8\}$, $\{01\bar{1}2\}$, $\{0001\}$ and $\{21\bar{3}4\}$ dry faces were already described in detail in our previous papers.[36,37,44,45] Here, we focus our attention on the structural modifications due to the presence of the solvent. In particular, we analyse the relaxed surface structures of the $\{10\bar{1}4\}$, $\{10\bar{1}0\}$, $\{01\bar{1}2\}$ and {0001} forms entering the equilibrium shape of the crystal, as it is discussed in the next paragraph.

In order to get some indications on how solvation affects the surface relaxation, we examine how much the z-coordinates of the uppermost Ca and C atoms change when the surface relaxes both in vacuum and in the presence of the solvent. Drawings representing the optimized surface structures are not reported here, since the modifications induced by water are not appreciable in a visual way. Nevertheless, for readers interested in a detailed structural analysis, GULP output files are freely available on the web page: http//mabruno.weebly.com/download.html.

On the $(10\bar{1}4)$ surface, it is found that the Ca atom in the outermost layer relaxes into the surface by 0.070 Å in vacuum, and by 0.074 Å in water, whereas the C atom moves outward by 0.113 Å in vacuum and by 0.100 Å in water.

On the $(10\bar{1}0)$ surface, a higher relaxation is observed, both in vacuum and with water. In fact, the Ca atom relaxes into the surface by 0.359 Å in vacuum and by 0.270 Å in water. The C atom moves inward by 0.174 Å in vacuum and by 0.172 Å in water.

In the case of the $CO_3$ terminated $(01\bar{1}2)$ face, a different behaviour is observed. We can distinguish two independent outermost Ca atoms. In the vacuum, a Ca atom relaxes into the surface by 0.169 Å, whereas the other one relaxes out of the surface by 0.110 Å. In water the displacements are slightly larger: one Ca moves inward by 0.182 Å and the other one moves outward by 0.135 Å. The C moves inward by 0.641 and 0.646 Å in vacuum and in water, respectively.

Very similar modifications are observed in case of the $CO_3$ terminated (0001) face. Calcium relaxes inward by 0.451 and 0.421 Å in vacuum and in water, respectively. Even Carbon relaxes inward both in vacuum and in water: 0.270 and 0.264 Å, respectively.

The $(10\bar{1}4)$, $(10\bar{1}0)$, $(01\bar{1}2)$ and (0001) surface structures are only slightly affected by the COSMIC parameters. Indeed, by performing the structure optimizations with (i) $\delta^{SC} = R_{solv} = 1$ Å, (ii) the default van der Waals radii implemented in GULP (2.75, 1.53 and 1.36 Å for Ca, C and O, respectively) and (iii) the van der Waals radius of Ca equals to 2.60 or 2.90 Å, we observe the following variations of the z-coordinates of the uppermost Ca and C atoms: 0.01, 0.10, 0.02 and 0.03 Å for the $(10\bar{1}4)$, $(10\bar{1}0)$, $(01\bar{1}2)$ and (0001) faces, respectively.

Experimental observations of the $(10\bar{1}4)$/water interface performed by Geissbühler et al.[46] by means of surface x-ray scattering, are in fairly good agreement with our calculations. Precisely, they stated that "…the heights of the outermost Ca and $CO_3$ ions are found to displace toward the bulk by 0.017 ± 0.004Å and -0.12 ± 0.01 Å, respectively".

On the contrary, our results do not agree with the theoretical data previously published by Perry et al.,[47] which performed MD simulations on the solvated $(10\bar{1}4)$ face at $T$ = 300K. They observed that water molecules strongly interact with the $(10\bar{1}4)$ calcite surface and attenuate the degree of relaxation usually associated with the calcite surface exposed in vacuum. They found that, for the $10\bar{1}4$ calcite layers closest to the water molecules, Ca ions are displaced out of the bulk position toward the aqueous phase by 0.12 ± 0.11 Å. A similar result was also obtained by Villegas-Jiménez et al.,[48] from *ab initio* calculations at Hartree-Fock level on $(\mathrm{CaCO3})_n$ clusters ($4 \leq n \leq 18$) solvated by $(H_2O)_n$ molecules ($2 \leq n \leq 6$). They found that the Ca atoms move out of the surface by 0.17 Å, whereas the C atoms move inward the surface by 0.05 Å.

### 3.2. The solvated surface energy and equilibrium shape at 0K

The solvated surface energies ($\gamma_{CF/w}^{0K}$) of the $\{10\bar{1}4\}$, $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, $\{01\bar{1}8\}$, $\{01\bar{1}2\}$, $\{0001\}$ and $\{21\bar{3}4\}$ faces are reported in Table 1; for comparison, the dry surface energies ($\gamma_{CF}^{0K}$) are also given. We only report and discuss the relaxed values of the surface energy, since, as demonstrated by Bruno et al.,[36] the unrelaxed surface energies calculated at empirical level are not physically grounded for calcite.

As expected, all of the $\gamma_{CF/w}^{0K}$ values are lower than the equivalent $\gamma_{CF}^{0K}$, since the solvent stabilizes the interfaces. However, it is a rather unexpected result the observation of such a slight reduction of the surface energies, corresponding to a mean value of 9.3% with a standard deviation (sd) of 1.4%: the highest reduction is observed for the $(01\bar{1}2)$ face (11.7%), whereas the lowest one is found for the $(01\bar{1}8)$ face (7.8%); this is fairly surprising when recalling that we are dealing with a markedly stepped face.

By applying the Gibbs–Wulff'stheorem[49] to the surface energy values of Table 1, we drawn the solvated and dry ES at 0K (Fig. 1). It is worth noting that the effect of water is rather moderate. In fact, by considering the morphological relevance index (MRI) for all {hkl} forms, defined as the percent ratio between the total area of the faces belonging to a {hkl} form and the total surface area of the crystal, we can observe that:

(i) water has a negligible effect on the $\{10\bar{1}4\}$ form, being the MRI for the solvated and dry crystal of 77.6% and 77.9%, respectively.

(ii) The MRI of the $\{01\bar{1}2\}$ form increases from 4.3% for the dry crystal to 7.9% for the solvated one; an opposite behavior is observed for the $\{10\bar{1}0\}$ form, for which the MRI decreases from 17.5 to 14.1%.

(iii) MRI does not significantly change for the {0001} form (0.3%).

In order to estimate how our results might be affected by the COSMIC parameters, we recalculated the solvated surface energies by considering: (i) $R_{solv} = \delta^{SC} = 1$ and van der Waals radius of Ca, C and O equal to 2.75, 1.53 and 1.36 Å (default radii implemented in GULP), respectively; (ii) $R_{solv} = \delta^{SC} = 1.4$ and van der Waals radius of Ca, C and O equal to 2.75, 1.53 and 1.36 Å, respectively; (iii) $R_{solv} = \delta^{SC} = 1.4$ and van der Waals radius of Ca, C and O equal to 2.60, 1.53 and 1.36 Å, respectively; (iv) $R_{solv} = \delta^{SC} = 1.4$ and van der Waals radius of Ca, C and O equal to 2.90, 1.53 and 1.36 Å, respectively; (v) $R_{solv} = \delta^{SC} = 1.4$ and van der Waals radius of Ca, C and O equal to 2.90, 1.70 and 1.52 Å, respectively. We set $R_{solv} = \delta^{SC} = 1$ since these are the values used by Klamt and Schüürmann[40] in their original paper describing the COSMO approach. In Table S1 (Supporting Information) the $\gamma_{CF/w}^{0K}$ values are given. Here, it is important to point out that the variations of equilibrium morphology are negligible, since the $\gamma_{CF/w}^{0K}$ values undergo a homogeneous variation: in the case (i) we have an average reduction of 13.4±1.6% with respect to the dry values, whereas in the case (ii) the average reduction is 11.0±1.8% and for the cases (iii), (iv) and (v) the average reduction is 14.2±1.9%, 7.9±1.8% and 7.3±1.6%, respectively. The variation of the others

COSMIC parameters was also tested, but not significant modifications of the $\gamma_{CF/w}^{0K}$ were observed. This demonstrates that the solvated ES of calcite at 0K is not affected by the COSMIC parameters. Therefore, even if a not correct choice of the computational parameters is done, the ES can be considered reliable.

**Table 1**. Anhydrous, $\gamma_{CF}^{0K}$, and hydrated, $\gamma_{CF/w}^{0K}$, surface energy values of the main crystal faces of calcite; the energy difference percentage between anhydrous and hydrated surface energies, Δ(%), is also reported. The calculations were performed with the Rohl et al.[12] calcite force field and the COSMIC method.

| Crystal face | $\gamma_{CF}^{0K}$ (J/m$^2$) | $\gamma_{CF/w}^{0K}$ (J/m$^2$) | $\Delta = (\gamma_{CF}^{0K} - \gamma_{CF/w}^{0K}) / \gamma_{CF}^{0K}$ (%) |
|---|---|---|---|
| $(10\bar{1}4)$ | 0.534[a] | 0.485 | -9.2 |
| $(11\bar{2}0)$ | 1.232[b] | 1.107 | -10.1 |
| $(10\bar{1}0)$ | 0.722[b] | 0.662 | -8.3 |
| $(01\bar{1}8)$ | 0.702[c] | 0.647 | -7.8 |
| $(21\bar{3}4)$ | 0.783[c] | 0.718 | -8.2 |
| (0001) | 0.711[d] | 0.640 | -10.0 |
| $(01\bar{1}2)$ | 0.750[e] | 0.662 | -11.7 |
| mean | 0.776 | 0.703 | -9.3 |
| sd | 0.216 | 0.192 | 1.4 |

[a]Rohl et al.;[12] [b]Massaro et al.;[45] [c]Aquilano et al.;[44] [d]Bruno et al.;[36] [e]Bruno et al.[37]

Unfortunately, the comparison between theoretical calculations (performed by considering free-defects ideal crystals) and experimental equilibrium morphologies of calcite is a very difficult task for the following reasons:

(i) *The experimental morphologies are always obtained at T > 0K, whereas our calculations were performed at T = 0K*. For a correct comparison between theoretical and experimental equilibrium morphologies, the knowledge of how the temperature affects the interface free energy values, and hence the crystal ES, is fundamental. This implies the ability to calculate the vibrational and configurational entropy of the different calcite/water interfaces at the temperature of the experiments (to obtain both equilibrium and growth shapes of calcite). An estimate of the changes due to temperature will follow in a subsequent section.

(ii) *Lacking of experimental equilibrium morphologies*. The very low solubility of calcite does not allow to observe, in a reasonable time, laboratory crystals in equilibrium with their pure mother solution. Indeed, laboratory experiments have never been performed, as far as we know. Moreover, equilibrium shapes of calcite (from micro-inclusions or from negative crystals, for instance) have never been observed in natural crystals, at the best of our knowledge.

(iii) *Lacking of information about the growth conditions of natural crystals*. Even assuming that natural crystals reached the equilibrium conditions, they did not nucleate and grow in a pure aqueous solution: several impurities, possibly acting as habit modifiers, were very likely present.

(iv) *Natural crystals are imperfect*. Even assuming that natural crystals grew in a pure aqueous solution and reached the equilibrium shape, at variance with simulated ideal crystals, they are certainly rich of point, linear and planar defects that could affect their interfacial energies and, as a consequence, their equilibrium morphology.

For all these reasons the reliability of our present and previous calculations cannot be judged on the basis of the natural or laboratory crystal morphologies that are always “growth morphologies” (we would like to stress here that *growth morphologies* are generally different from the *equilibrium* ones). However, it is possible to apply simple thermodynamic considerations for testing the ability of the different calcite and water force fields to reproduce the equilibrium crystal shape. Nevertheless the temperature dependence of the dry surface energy should be preliminarily discussed.

**Figure 1**. (a) Solvated and (b) dry equilibrium shape of calcite at 0K.

### 3.3. Critical review of published dry and solvated equilibrium morphology at 0K

In the past, several force fields to study $CaCO_3$ polymorphs, both in anhydrous and aqueous conditions, have been developed; for an interesting review and discussion on all these force fields see the work by Raitieri et al.[18] However, it is worth noting that the focus of the majority of these previous studies was to obtain an accurate description of the solid-state properties of this substance, with particular emphasis on the bulk structure, mechanical hardness and phonon spectra. Nevertheless, even if these force fields were suitably conceived to reproduce and study the bulk properties, they were also widely applied to the study of the structure of the crystal surfaces and to determine the dry and solvated surface energies. In particular, the majority of these studies were devoted to the $\{10\bar{1}4\}$ form, which was usually believed to be the main form of the natural calcite crystals. Instead, as reported by Aquilano et al.,[44] the occurrence frequency of the main crystallographic forms of natural calcite crystals is the following: $\{10\bar{1}0\}$ 46.3%, $\{21\bar{3}4\}$ 38.9%, $\{01\bar{1}8\}$ 37.2%, $\{10\bar{1}4\}$ 35.7%, $\{01\bar{1}2\}$ 24.2%, $\{10\bar{1}1\}$ 23.8%, $\{0001\}$ 17.2% and $\{11\bar{2}0\}$ 14.1%. Likely, the $\{10\bar{1}4\}$ form could be the dominant one when calcite grows from pure aqueous solution at low temperature and supersaturation. However, natural crystals grown under variable conditions of temperature and supersaturation (especially in the presence of inorganic and organic impurities) exhibit a greater variety of shapes.

The $\{10\bar{1}0\}$, $\{11\bar{2}0\}$ and $\{0001\}$ forms were also frequently studied, as it results from Table S2 (Supporting Information); in Table S2 all the previous calculated dry and solvated surface energy values of the $\{10\bar{1}4\}$, $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, $\{01\bar{1}8\}$, $\{01\bar{1}2\}$, $\{0001\}$ and $\{21\bar{3}4\}$ relaxed faces are also reported. In order to get an overall view of these data, they have been plotted in Fig. 2. We remark that no calculations of the solvated surface energies of the $\{01\bar{1}8\}$ and $\{21\bar{3}4\}$ faces were performed until now, though their knowledge would be a matter of utmost importance in the biomineralization processes involving calcite (see Aquilano et al.[44] and references therein).

**Figure 2**. Spreading of computed (a) dry, $\gamma_{CF}^{0K}$, and (b) solvated, $\gamma_{CF/w}^{0K}$, surface energy values of the main crystal faces of calcite. The black dots represent the values found in the scientific literature (see Table S2, where all the values and references are reported); the red dots represent the values calculated with the Rohl et al.[12] calcite force field and the COSMIC method.

It is instructive to reproduce the ES at 0K by using the $\gamma_{CF}^{0K}$ and $\gamma_{CF/w}^{0K}$ values previously calculated by other authors (see Figs. S1 and S2 in the Supporting Information). From an accurate analysis of the previous works on dry calcite we can observe that:

(i) the $\{10\bar{1}4\}$ form is present in all of the ESs.

(ii) The $\{01\bar{1}2\}$ form only appears in the ESs determined at *ab initio* level with the PBE Hamiltonian,[35] this finding being in very close agreement with the previous *ab initio* calculations (B3LYP Hamiltonian) performed by Bruno et al.[37]

(iii) The $\{10\bar{1}0\}$ form enters the ES reproduced by means of the PBE Hamiltonian, and the force fields developed by Hwang et al.,[7] Pavese et al.[13] and Jackson and Price;[17]

(iv) the $\{11\bar{2}0\}$ form is only present in the ES obtained with the Jackson and Price[17] force field.

(v) The ESs obtained with the Braybrook et al.[14] and Parker et al.[16] force fields, only show the $\{10\bar{1}4\}$ form.

At variance with the dry case cited above and our COSMIC calculations, the previous hydrated ESs only show the $\{10\bar{1}4\}$ form;[6,9,11] they were determined at empirical level (force fields for calcite and water) and by considering an adsorbed layer of water onto the different calcite surfaces.

### 3.4. The dry surface free energy at *T* > 0K

Up to now, we have considered the dry surface energy at $T = 0$K, but it is important to know how this quantity changes with temperature ($T > 0$K) by taking into account the entropic contribution due to (i) the vibrational motion of atoms in the bulk crystal and at its surface (vibrational entropy) and (ii) the different surface configurations of the crystal face (configurational entropy). The effect of the temperature on the dry surface energy values is not negligible, as recently demonstrated for NaCl and LiF.[50-52] As a matter of fact, *ab initio* calculations performed at DFT level[50] on the (100) face of LiF have shown that the value of the dry surface energy decreases by ~13% by increasing the temperature from $T = 0$ to $T = 300$K. Furthermore, theoretical works[51,52] performed on NaCl crystals (halite) have reported, in the same temperature interval, a very similar decrease of the dry surface energy values of the {100}, {110} and {111} faces.

#### 3.4.1. Computational methods for determining the dry surface free energy at *T* > 0K

Before discussing the case of calcite, a thermodynamic relation is recollected including all of the terms contributing to the dry surface free energy of a crystal face *CF*, $\gamma_{CF}^{T}$, at the temperature *T*:

$$\gamma_{CF}^{T} = \gamma_{CF}^{0K} + \gamma_{CF}^{T,vib} + \gamma_{CF}^{T,config} \quad (2)$$

where $\gamma_{CF}^{0K}$ is the dry surface energy at $T$ = 0K (the specific work needed for creating and relaxing a dry crystal face at 0K); $\gamma_{CF}^{T,vib}$ is the vibrational (thermal) contribution (the specific internal vibrational energy and vibrational entropy at the temperature $T$, including zero point energy contribution); $\gamma_{CF}^{T,config}$ is the specific surface configurational entropy, which is related to the number of possible configurations of the surface and is given by the Boltzmann entropy formula, $\gamma_{CF}^{T,config} = -(kT\ln W)/A$, where $W$ is the number of the surface configurations.

The thermal contribution $\gamma_{CF}^{T,vib}$ can be accurately evaluated by calculating, at the *ab initio* level, the frequencies of the vibrational modes for the bulk crystal and the slab limited by the faces of interest.[50] This allows to calculate the vibrational partition function for the slab and the bulk crystal, $Z_{slab/bulk}^{vib} = \sum_i \sum_k e^{-\frac{h\nu_{i,k}}{2kT}} \Big/ \left(1 - e^{-\frac{h\nu_{i,k}}{kT}}\right)$ and, as a consequence, the vibrational energy ($E_{slab/bulk}^{vib}$) and entropy ($S_{slab/bulk}^{vib}$) of the slab and bulk crystal:

$$\begin{aligned} E_{slab/bulk}^{vib} &= kT^2\left(\frac{\partial}{\partial T}\ln Z_{slab/bulk}^{vib}\right) \\ S_{slab/bulk}^{vib} &= k\left(T\frac{\partial}{\partial T}\ln Z_{slab/bulk}^{vib} + \ln Z_{slab/bulk}^{vib}\right) \end{aligned} \quad (3)$$

where $h$ and $k$ are the Planck and Boltzmann constants, respectively, and $\nu_{i,k}$ is the frequency of the $i^{th}$ vibrational mode at the $k^{th}$ point in the Brillouin zone, in the slab or bulk crystal. Then, the vibrational contribution to the surface energy is obtained through the relation:

$$\gamma_{CF}^{T,vib} = \frac{E_{slab}^{vib} - E_{bulk}^{vib}}{A} - T\,\frac{S_{slab}^{vib} - S_{bulk}^{vib}}{A} \quad (4)$$

Unfortunately, *ab initio* calculations for the determination of $\gamma_{CF}^{T,vib}$ are very expensive from the computational point of view; thus, they were performed on very simple systems only, such as LiF, and no quantum-mechanical estimates of $\gamma_{CF}^{T,vib}$ for the crystal faces of calcite do exist.

An alternative method for determining the dry surface free energy at the temperature of interest is provided by the molecular dynamics (MD):[53] the average partition function of the canonical ensemble, $\langle Q(N,V,T)\rangle$, must be calculated for the elapsed time of the simulation. The free energy of the slab ($F_{slab}$) and bulk crystal ($F_{bulk}$) at the temperature of interest is obtained from the relation $F_{slab/bulk} = -kT\ln\langle Q(N,V,T)\rangle_{slab/bulk}$ that allows the estimation of the dry surface free energy by applying the equation $\gamma_{CF}^{T} = (F_{slab} - F_{bulk})/A$. However, the only two works reporting MD simulations of dry calcite surfaces at $T$ = 300K[1,54] were performed by averaging the potential energy of the system, $\langle U \rangle_{slab/bulk}$, and not the partition function $\langle Q(N,V,T) \rangle$, neglecting in this way the vibrational and configurational entropic contributions. Furthermore, there is not agreement between the dry surface energy values reported in these works: Kvamme et al.[1] give 0.860 and 1.500 J/m$^2$ for the $(10\bar{1}4)$ and $(10\bar{1}0)$ faces, respectively, whereas 0.520 and 0.870 J/m$^2$ are the values reported by Parker et al.[54]

### 3.4.2. The $(10\bar{1}4)$ dry surface free energy at $T$ > 0K

As reported above, no *ab initio* estimates of $\gamma_{CF}^{T,vib}$ for the crystal faces of calcite do exist. Despite that, we can derive a thorough estimate of the dry surface free energy of the $(10\bar{1}4)$ face of calcite at 300K, $\gamma_{(10\bar{1}4)}^{300K}$, by (i) using the very precise values of the dry surface energy at $T$ = 0K of the $(10\bar{1}4)$ face, $\gamma_{(10\bar{1}4)}^{0K}$, obtained at *ab initio* level by Bruno et al.[36] and Akiyama et al.:[35] 0.503 and 0.510 J/m$^2$, respectively (which are well reproduced by the Rohl potential, 0.534 J/m$^2$), and (ii) doing some assumptions on the $\gamma_{(10\bar{1}4)}^{300K,vib}$ and $\gamma_{(10\bar{1}4)}^{300K,config}$ values.

Concerning item (i), an estimate of $\gamma_{(10\bar{1}4)}^{0K}$ is given by the averaged value: $(0.503 + 0.510 + 0.534)/3 =$ 0.515 ± 0.016 J/m$^2$. Instead, as concerns item (ii), since $\gamma_{(10\bar{1}4)}^{300K,vib}$ has never been calculated, we can only provide an approximate estimate of such contribution, by taking advantage of the analogy with the very compact (100) face of LiF, for which the vibrational energy and entropy at 300K were determined at *ab initio* level.[50] On the ground of such analogy, we assume $\gamma_{(10\bar{1}4)}^{300K,vib} = -0.1 \times \gamma_{(10\bar{1}4)}^{0K} =$ -0.051 ± 0.002 J/m$^2$ to be a reasonable estimate. Finally, the configurational entropy of the crystal surface, $\gamma_{(10\bar{1}4)}^{300K,config}$, must be also taken into account. However, according to the Hunt and Gale's model,[55] the configurational entropy of a (100) face of a mono-atomic face centered cubic (fcc) crystal, that is a very compact face like the $(10\bar{1}4)$ one of calcite, only reduces the surface energy by∼5% at the melting temperature. Therefore, we may neglect this contribution to the $(10\bar{1}4)$ free surface energy as, at 300K, it is probably lower than the error introduced in our estimates of the atomic vibrational effect on the energy. Now, by inserting $\gamma_{(10\bar{1}4)}^{0K}$ and $\gamma_{(10\bar{1}4)}^{300K,vib}$ in eq. (2), we obtain $\gamma_{(10\bar{1}4)}^{300K}$ = (0.515 ± 0.016) + (-0.051 ± 0.002) = 0.464 ± 0.018 J/m$^2$. It is not possible to extend this reasoning to other faces of calcite since there are not precise estimates of the terms entering in eq. (2). In the following we will use the result reported above to derive and discuss the free energy of the interface $(10\bar{1}4)$/water at 300K.

In principle, the vibrational contribution could also be evaluated at an empirical level by employing a suitable force field and eq. (4). We tried to apply the Rohl potential for this purpose, but we obtained physically grounded values only for the $(10\bar{1}4)$ slab, whereas for the other faces the slab entropy was lower than the bulk one and, therefore, the vibrational contribution cannot be evaluated. We calculated the $(10\bar{1}4)$ slab and bulk entropy of calcite at $T$ = 300K, by respecting the convergence criteria on the number of $k$ points and the slab thickness. Then, we obtained $\gamma_{(10\bar{1}4)}^{300K,vib}$ = -0.030 J/m$^2$ , a value which is consistent with our estimate reported above.

### 3.5. The free energy of the $(10\bar{1}4)$/water interface at $T$ = 300K

We are able to determine the free energy of the $(10\bar{1}4)$/water interface at 300K, $\gamma_{(10\bar{1}4)/w}^{300K}$, by means of the Young's relation:

$$\gamma_{(10\bar{1}4)/w}^{300K} = \gamma_{(10\bar{1}4)}^{300K} - \gamma_{w}^{300K} \times \cos\theta \quad (5)$$

where $\gamma_{w}^{300K}$ = 0.072 J/m$^2$ is the water/vapor interfacial free energy at 300K[56] and $\theta$ = 44.7° ± 3.4° is the contact angle between calcite $(10\bar{1}4)$ and water that we measured at room temperature (see Supporting Information for details on the experimental setting); the contact angle is the angle between the surface of a solid substrate and the outline tangent to a drop deposited on it. Now, by inserting our $\gamma_{(10\bar{1}4)}^{300K}$ value in the Young's relation, one obtains $\gamma_{(10\bar{1}4)/w}^{300K}$ = 0.412 ± 0.020 J/m$^2$.

#### 3.5.1. Validation of our estimate of the free energy of the $(10\bar{1}4)$/water interface and comparison with the previous published data

We can demonstrate through the Dupré's relation:[57]

$$\gamma_{(10\bar{1}4)/w}^{300K} = \gamma_{(10\bar{1}4)}^{300K} + \gamma_{w}^{300K} - \beta_{adh} \quad (6)$$

that the estimated value of $\gamma_{(10\bar{1}4)/w}^{300K}$ is physically consistent; $\beta_{adh}$ is the water adhesion energy with the solid substrate, i.e.: the specific energy gained by adding a water drop above the crystal surface. Indeed, by inserting the Young's equation in (6), one obtains $\beta_{adh} = \gamma_{w}^{300K}(1+\cos\theta)$. By assuming the limiting case of a perfect wetting ($\theta$ = 0°), the highest value of the adhesion energy should be $\beta_{adh} = 2\gamma_{w}^{300K}$ = 0.144 J/m$^2$, whereas in the case of a perfect hydrophobic material ($\theta$ = 180°), $\beta_{adh}$ = 0. It is worth noting that these boundaries are valid for all the crystal surfaces wetted by water at 300K. Now, by inserting the values of $\gamma_{(10\bar{1}4)/w}^{300K}$, $\gamma_{(10\bar{1}4)}^{300K}$ and $\gamma_{w}^{300K}$ in eq. (6), one obtains: $\beta_{adh}$ = 0.124 ± 0.038 J/m$^2$ < 0.144 J/m$^2$, which not only is consistent with the constraint imposed by the relation, but it is also a very reasonable value, having taken into account the evident wetting observed at the calcite/water interface.

Significant scatter of the values of $\gamma_{(10\bar{1}4)/w}^{300K}$ is observed in the measured free surface energies of calcite, by using different experimental methods (see Forbes et al.,[58] for a detailed review of the experimental data and methods). Homogeneous and heterogeneous nucleation studies give very low values in the range 0.032–0.085 J/m$^2$, whereas the surface energy values obtained by heat of immersion technique are found to be 0.54–1.48 J/m$^2$. Finally, earlier experimental works based upon wetting and contact angle report 0.072-0.098 J/m$^2$.

A wide range of values (0.090-0.387 J/m$^2$) is also found in computational works where MD simulations were carried out to study the $(10\bar{1}4)$ calcite/water interface.[1,2,4,7]

However, by considering relation (6) together with the well-established value of $\gamma_w^{300K}$ = 0.072 J/m$^2$ and our estimate of $\gamma_{(10\bar{1}4)}^{300K}$ = 0.464 ± 0.018 J/m$^2$, we can state with a certain degree of accuracy that all these computational and experimental values of $\gamma_{(10\bar{1}4)/w}^{300K}$ are not acceptable on a physical ground. As a matter of fact, once the values determined by means of MD simulations, nucleation experiments and contact angle measurements are inserted in relation (6), one finds $\beta_{adh} > 0.144$ J/m$^2$, which is physically inconsistent, since it is theoretically expected from the coupling of Young's and Dupré's relations that the adhesion energy of a 3D condensed phase on a substrate cannot be larger than its cohesion energy $\kappa = 2\gamma$. On the contrary, if the calorimetric literature data are considered, it turns out that $\beta_{adh} < 0$.

**Figure 3.** The IAP/K$_{sp}$ ratio as a function of critical step length (l) on growth spirals of the $\{10\bar{1}4\}$ faces. The red line and shaded area were drawn by considering $\bar{\gamma}$ = 0.330 J/m$^2$ and $\bar{\gamma} = \gamma_{(10\bar{1}4)/w}^{300K}$ = 0.412 ± 0.020 J/m$^2$, respectively, in eq. (7).

A further evidence of the soundness of our estimate of $\gamma_{(10\bar{1}4)/w}^{300K}$ is given by the work by Fan et al.,[59] on the dependence of the calcite solubility on grain size. They measured (at room temperature), by means of the atomic force microscope, the critical step lengths ($l$) on growth spirals of the $\{10\bar{1}4\}$ faces at different supersaturation $\Omega = IAP/K_{sp}$, where $IAP$ is the ionic activity product of $Ca^{2+}$ and $CO_3^{2-}$ in the solution and $K_{sp} = 10^{-8.48}$ is the solubility product of calcite at room temperature. Then, they reproduced the experimental ($IAP$ vs. $l$) data by means of a simplified version of the Gibbs-Thomson equation[60] (red line in Fig. 3):

$$IAP / K_{sp} = \exp(c/l) \quad (7)$$

where $c = (2\tau W\bar{\gamma})/(3\rho RT)$; $\tau$ = 6.135 is the geometrical factor for the rhombohedra; $W$ is the molecular weight of $CaCO_3$; $\rho$ = 2.71 g/cm$^3$ is the density of the crystal; $R$ is the gas constant; $\bar{\gamma}$ = 0.330 J/m$^2$ is the mean surface free energy. The $\bar{\gamma}$ value considered by Fan et al.[59] was calculated at empirical level by De Leeuw[61] for a hydrated $(10\bar{1}4)$ surface at 0K, but the experimental measurements were performed at room temperature. Therefore, we introduced our estimate of $\gamma_{(10\bar{1}4)/w}^{300K}$ = 0.412 ± 0.020 J/m$^2$ into eq. (7) and obtained the shaded area reported in Fig. 3. Interestingly, we observe that the experimental data, which are not reported in Fig. 3 because Fan et al.[59] only gave a plot (see Fig. 4, pag. 3824 of their paper) without quoting the corresponding numerical values in a table, are better fitted with our estimate of $\gamma^{300K}_{(10\bar{1}4)/w}$ than with the surface energy considered by Fan et al.[59] In order to give an idea, at $\Omega = 2.0$ the measured step length is in the values range of ~32-48 nm, whereas the eq. (7) gives the values of ~30 and ~35-38 nm for $\bar{\gamma}$ = 0.330 and $\bar{\gamma}$ = 0.412 ± 0.020 J/m$^2$, respectively.

### 3.6. A rough estimate of the vibrational and configurational entropy of the $(10\bar{1}4)$/water interface at *T* = 300K

The free energy of the $(10\bar{1}4)$/water interface at 300K, $\gamma^{300K}_{(10\bar{1}4)/w}$, can be written as follow:

$$\gamma^{300K}_{(10\bar{1}4)/w} = \gamma^{0K}_{(10\bar{1}4)/w} + \gamma^{300K,vib}_{(10\bar{1}4)/w} + \gamma^{300K,config}_{(10\bar{1}4)/w} \quad (8)$$

where $\gamma^{0K}_{(10\bar{1}4)/w}$ is the solvated surface energy calculated with the COSMIC approach at 0K (the values obtained with the different computational parameters are reported in Table S1), $\gamma^{300K,vib}_{(10\bar{1}4)/w}$ is the vibrational contribution to the free interface energy (specific interface vibrational energy and vibrational entropy) and $\gamma^{300K,config}_{(10\bar{1}4)/w}$ is the specific interface configurational entropy, which is related to the number of possible configurations of the water molecules on the $(10\bar{1}4)$ face. By inserting $\gamma^{0K}_{(10\bar{1}4)/w}$ = 0.478 ± 0.018 J/m$^2$ (the average value of those reported in Table S1) and $\gamma^{300K}_{(10\bar{1}4)/w}$ = 0.412 ± 0.020 J/m$^2$ in eq. (8), one obtains $\left(\gamma^{300K,vib}_{(10\bar{1}4)/w} + \gamma^{300K,config}_{(10\bar{1}4)/w}\right)$ = -0.066 ± 0.038 J/m$^2$, an estimate of the vibrational energy and entropic contribution to the free energy at 300K of the $(10\bar{1}4)$/water interface. This means that $\left(\gamma^{300K,vib}_{(10\bar{1}4)/w} + \gamma^{300K,config}_{(10\bar{1}4)/w}\right)$ reduces by ~14% the solvated surface energy value calculated at 0K. It is likely that the $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, $\{01\bar{1}8\}$, $\{01\bar{1}2\}$, $\{0001\}$ and $\{21\bar{3}4\}$ faces suffer a higher modification, but, at the present time, we are not able to estimate the relevant energy reductions since reliable $\gamma^{300K}_{CF/w}$ values are lacking.

At variance with the surface structures and the ES previously discussed, this estimate is strongly dependent by the COSMIC parameters, as deduced by observing the $\gamma^{0K}_{(10\bar{1}4)/w}$ values listed in Table S1: such values are in the range of 0.453-0.497 J/m$^2$. For this reason we carried out the calculation of $\gamma^{0K}_{(10\bar{1}4)/w}$ by considering a wide range of values of the COSMIC parameters (see Computational details) and inserted into eq. (8) its average value.

### 3.7. Some considerations on homogeneous and heterogeneous calcite nucleation in aqueous solution

Now, we are able to do some considerations on the classical nucleation theory (CNT) of calcite in aqueous solution, on the basis of our estimate of $\gamma^{300K}_{(10\bar{1}4)/w}$. According to CNT, the free energy change occurring during the homogeneous nucleation of $\{10\bar{1}4\}$ rhombohedra ($\Delta G_{\mathrm{hom}}$) at $T$ = 300K in aqueous solution is given by:[57]

$$\Delta G_{\mathrm{hom}} = -\left(\frac{f_{\{10\bar{1}4\}}L^3}{V_{CaCO_3}}\right)\Delta\mu + f_{\{10\bar{1}4\}}\left(6L^2\right)\gamma^{300K}_{(10\bar{1}4)/w} \quad (9)$$

where $L$ is the length of the edge of the rhombohedra, $f_{\{10\bar{1}4\}}$ = 0.978 is the shape factor for the $\{10\bar{1}4\}$ rhombohedra, $V_{CaCO_3}$ = 61.13×10$^{-30}$ m$^3$ is the molecular volume of the growth unit $CaCO_3$ and $\Delta\mu = kT\sigma = kT\ln\left(IAP/K_{sp}\right)$ is the thermodynamical supersaturation. It is important to stress that relation (9) is grounded on the capillarity approximation: to be more precise, $\gamma^{300K}_{(10\bar{1}4)/w}$ is considered constant for every crystal size. In Fig. 4a we report $\Delta G_{\mathrm{hom}}/kT$ as a function of $L$ for $\sigma$ = 3.5 (black lines) and $\sigma$ = 4.0 (red lines), in order to compare our values with those recently obtained by Hu et al.,[30] which applied eq. (9) by considering an interface energy of 0.109 J/m$^2$. Unfortunately, the energy value used by Hu et al.[30] was experimentally determined for $BaCO_3$ by Söhnel and Mullin,[62] which instead estimated 0.083 J/m$^2$ for $CaCO_3$. However, according to our discussion in the paragraph 3.5, both values are not acceptable on a physical ground and, therefore, this mistake is not particularly significant for the analysis that follows.

The critical size of the nucleus ($L^{cr}_{\mathrm{hom}}$), corresponding to the maximum of the function $\Delta G_{\mathrm{hom}}$, is determined by equaling to zero the derivative of eq. (9) with respect to $L$: $L^{cr}_{\mathrm{hom}} = 4V_{CaCO_3}\gamma^{300K}_{(10\bar{1}4)/w}/\Delta\mu$, which is equal to ~6.9 ± 0.3 and ~6.1 ± 0.3 nm for $\sigma$ = 3.5 and 4.0, respectively. $\Delta G^{cr}_{\mathrm{hom}}$, the thermodynamic barrier to overcome for stabilizing the critical nuclei, i.e. the value of $\Delta G_{\mathrm{hom}}$ when $L$ = $L^{cr}_{\mathrm{hom}}$, is $\Delta G^{cr}_{\mathrm{hom}}/kT$ = ~9.4×10$^3$ ± 1.3×10$^3$ and ~7.2×10$^3$ ± 1.0×10$^3$ for $\sigma$ = 3.5 and 4.0, respectively (see Fig. 4a). $L^{cr}_{\mathrm{hom}}$ and $\Delta G^{cr}_{\mathrm{hom}}/kT$ estimated by Hu et al.[30] are 1.85 nm and 0.175×10$^3$ when $\sigma$ = 3.5. Hence, these values are very significantly lower (by about one order of magnitude) with respect to the ones we obtained with a new estimate of the interface energy.

In the case of the heterogeneous nucleation, the free energy change occurring during the formation of a $\{10\bar{1}4\}$ rhombohedron on a substrate ($\Delta G_{het}$) at $T$ = 300K in aqueous solution is given by:[57]

$$\Delta G_{het} = \Delta G_{\mathrm{hom}} - f_{\{10\bar{1}4\}}L^2\beta_{adh} \quad (10)$$

where $\beta_{adh}$ is the calcite adhesion energy with a solid substrate; as previously discussed for the $(10\bar{1}4)$/water interface and according to the Dupré's and Young relations, it turns to be: $0 \leq \beta_{adh} \leq 2\gamma^{300K}_{(10\bar{1}4)/w}$. When $\beta_{adh}$= 0, eq. (10) reduces to eq. (9), i.e. to the case of the homogeneous nucleation.

By increasing $\beta_{adh}$, both the size of the critical nucleus ($L_{het}^{cr}$) and the value of the thermodynamic barrier ($\Delta G_{het}^{cr}$) decrease. For the sake of simplicity, in the following we only discuss the most favorable condition for having heterogeneous nucleation, that is $\beta_{adh}$ = $2\gamma^{300K}_{(10\bar{1}4)/w}$. In this case, $L_{het}^{cr} = V_{CaCO_3}\left(12\gamma^{300K}_{(10\bar{1}4)/w} - 2\beta_{adh}\right)\big/\left(3\Delta\mu\right)$ is 4.6 ± 0.3 and 4.1 ± 0.3 nm for $\sigma$ = 3.5 and $\sigma$ = 4.0 (Fig. 4b), respectively. In the same way: $\Delta G_{het}^{cr}\big/kT$ is $2.8\times10^3 \pm 0.5\times10^3$ and $2.1\times10^3 \pm 0.4\times10^3$ for $\sigma$ = 3.5 and $\sigma$ = 4.0.

By analyzing the values of $\Delta G_{het}^{cr} / kT$, we point out that it should be very difficult to have calcite nucleation when supersaturation is consistent with experimental observations, i.e. a very high classical barrier must be overcome for obtaining a nucleus of critical size. Therefore, in the light of the calculations reported above, we consider to be highly probable the fact that calcite crystallization proceeds throughout the formation of an amorphous calcium carbonate (ACC) which would act as a precursor phase.[63] Then, it is equally probable that ACC can form with an activation barrier negligible compared to that we estimated for calcite by means of the CNT.

**Figure 4**. The free energy change, as a function the length ($L$) of the edge of the $\{10\bar{1}4\}$ rhombohedron, during homogeneous ($\Delta G_{\mathrm{hom}}$) and heterogeneous ($\Delta G_{het}$) classical nucleation. It is worth noting the lowering of the activation barrier and of the critical size of the nucleus when going from homogeneous to the heterogeneous nucleation.

## 4. Conclusions

In this work a detailed analysis on the dry and solvated ES of calcite crystals at 0K was performed. New solvated energy values at 0K of the main crystal faces were calculated and critically compared to the previous ones. Finally, the temperature effect on the solvated energy was analyzed. In detail, the results we obtained can be summarized as follows:

(i) the presence of water reduces by ~7-14% (see Tables 1 and S1), in a homogeneous way, the dry surface energy at 0K of the $\{10\bar{1}4\}$, $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, $\{01\bar{1}8\}$, $\{01\bar{1}2\}$, $\{0001\}$ and $\{21\bar{3}4\}$ forms. Hence, the solvated and dry ES at 0K result to be nearly homothetic: in both cases the $\{10\bar{1}4\}$, $\{10\bar{1}0\}$, $\{01\bar{1}2\}$ and $\{0001\}$ forms are present. We can interpret these results as a consequence of a weak and un-localized interaction between the water molecules and the different faces of calcite.

(ii) The free surface energy at 300K of the dry $(10\bar{1}4)$ face, $\gamma^{300K}_{(10\bar{1}4)}$, is estimated to be 0.464 ± 0.018 J/m$^2$. This value can be used as a constraint when developing new calcite force fields for MD simulations or for testing their effectiveness.

(iii) The free energy of the $(10\bar{1}4)$/water interface, $\gamma^{300K}_{(10\bar{1}4)/w}$, and its water adhesion energy, $\beta_{adh}$, at $T$ = 300K are 0.412 ± 0.020 and 0.124 ± 0.038 J/m$^2$, respectively. As the $\{10\bar{1}4\}$ form has the lowest free interface energy and then is the most stable one for calcite, $\gamma^{300K}_{(10\bar{1}4)/w}$ = 0.412 ± 0.020J/m$^2$ can be considered as the lower limit for the free energy of the other $\{\, hk\bar{i}l \,\}$ crystal forms: this means that both experimental and theoretical estimates of the free energy of other forms of calcite obeying to the relation $\gamma^{300K}_{(hk\bar{i}l)/w} \leq \gamma^{300K}_{(10\bar{1}4)/w}$ must be considered physically meaningless. Accordingly, the interface energies values of 0.220, 0.270, 0.370 and 0.250 J/m$^2$, calculated for the (10$\bar{1}$0), (11$\bar{2}$0), (01$\bar{1}$2) and (0001) faces, respectively, by means of MD simulations at 300K by Duffy and Harding,[4] are unrealistic (Table S2). Furthermore, our estimate can be used for developing or testing the empirical force fields describing the calcite/water interactions.

(iv) A rough estimate of the vibrational energy and entropy ($\gamma^{300K,vib}_{(10\bar{1}4)/w}$), and configurational entropy ($\gamma^{300K,config}_{(10\bar{1}4)/w}$) of the (10$\bar{1}$4)/water interface at 300K has been obtained: $\left(\gamma^{300K,vib}_{(10\bar{1}4)/w} + \gamma^{300K,config}_{(10\bar{1}4)/w}\right)$ = -0.066 ± 0.038 J/m$^2$; then, the solvated surface energy at 0K ($\gamma^{0K}_{(10\bar{1}4)/w}$ = 0.478 ± 0.018 J/m$^2$) is reduced by ~14% at 300K. At the best of our knowledge, this is the first time that such a thermodynamical quantity has been calculated for a face of calcite. It is reasonable to expect a higher entropic contribution and, therefore, a higher reduction of the solvated energy for the (10$\bar{1}$0), (11$\bar{2}$0), (01$\bar{1}$8), (01$\bar{1}$2), (0001) and (21$\bar{3}$4) faces. Thus, an increase of the morphological importance of the (10$\bar{1}$0), (01$\bar{1}$2) and (0001) faces is possible and in particular, the {01$\bar{1}$8} and {21$\bar{3}$4} forms could enter the solvated equilibrium morphology. Obviously, in order to confirm this hypothesis, more detailed calculations on the vibrational and configurational entropy have to be performed.

(v) Finally, by applying the CNT, we estimated the thermodynamic barrier $\Delta G^{cr}_{\mathrm{hom}} / kT$ = ~9.4×10$^3$ ± 1.3×10$^3$ and ~7.2×10$^3$ ± 1.0×10$^3$ for $\sigma$ = 3.5 and 4.0, in the case of homogeneous nucleation, and $\Delta G^{cr}_{het} / kT$ = 2.8×10$^3$ ± 0.5×10$^3$ and 2.1×10$^3$ ± 0.4×10$^3$ when $\sigma$ = 3.5 and $\sigma$ = 4.0, for heterogeneous nucleation. Such extremely high values should prevent the direct formation of calcite. Then, our calculations support previous experimental[63] and theoretical evidences[64,65] that calcite formation should proceed throughout the early formation of an amorphous calcium carbonate (ACC) which should require a fairly lower, or even null, activation energy with respect to a crystalline calcium carbonate polymorph; larger nanoparticles of ACC can ultimately undergo a transition to a crystalline phase. This hypothesis should not be surprising, if one remembers that Nature offers an analogous example when dealing with the $SiO_2$ system: in fact the precipitation of the amorphous compound $SiO_2 \cdot nH_2O$ (silica, for mineralogists) is largely favored with respect to anyone of the crystallized polymorphic anhydrous $SiO_2$ (e. g., α-quartz, tridimite, crystobalite).

**Supporting Information Available.** Dry and solvated relaxed surface energies at 0K of the main faces of calcite ({10$\bar{1}$4}, {10$\bar{1}$0}, {11$\bar{2}$0}, {01$\bar{1}$8}, {01$\bar{1}$2}, {0001} and {21$\bar{3}$4}) (Table S1) calculated by means of the Rohl et al.[12] force field and by considering different COSMIC parameters: (i) $R_{solv} = \delta^{SC}$ =1, r(Ca) = 2.75 Å, r(C) = 1.53 Å, r(O) = 1.36 Å; (ii) $R_{solv} = \delta^{SC}$ =1.4, r(Ca) = 2.75 Å, r(C) = 1.53 Å, r(O) = 1.36 Å; (iii) $R_{solv} = \delta^{SC}$ =1.4, r(Ca) = 2.75 Å, r(C) = 1.70 Å, r(O) = 1.52 Å; r(Ca), r(C) and r(O) are van der Waals radii of Ca, C and O, respectively; (iv) $R_{solv} = \delta^{SC} = 1.4$ and van der Waals radius of Ca, C and O equal to 2.90, 1.53 and 1.36 Å, respectively; (v) $R_{solv} = \delta^{SC} = 1.4$ and van der Waals radius of Ca, C and O equal to 2.90, 1.70 and 1.52 Å, respectively. A summary of computed hydrated and anhydrous calcite surface energies (Table S2) previously published by other authors. Drawings of dry and solvated calcite equilibrium shapes at $T$ = 0K and $T$ = 300K, obtained by using the surface energy values reported in Table S2. Description of the experimental setting for the measurement of the contact angle between calcite $(10\bar{1}4)$ and water at room temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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