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A new calculation strategy to analyze the vibrational free energy of a slab and calculate the vibrational contribution of the surface free energy

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Summary: We developed a new calculation strategy for determining the vibrational contribution of each layer or atom forming a slab, where the latter is a two-dimensional periodic structure of given thickness, generated by separating the bulk structure along the *hkl* plane of interest and used to simulate the crystal surfaces. By means of this new calculation methodology, it is now possible to estimate how the surface free energy of a crystal face changes with temperature by only taking into account the entropic contribution due to the vibrational motion of atoms in the slab. Furthermore, the model is extended to the calculation of the vibrational contribution to the free energy of the interface between (ii) two identical crystals in twinning relationship and (ii) two different crystals in epitaxial relationship.

Our model uses the frequencies of the vibrational modes of a slab and it is based on the construction of a weight function taking into account how the vibrational amplitude of the atoms involved in the vibrational mode is modified by the presence of the surface.

We applied the model to the following systems: (i) 28-layer (100) slab of LiF and (ii) 10-layer (10.4) slab of calcite ($CaCO_3$). In both cases, the vibrational energy, vibrational entropy and vibrational free energy of the optimized slab, and the contribution to these quantities of each atom and layer forming the slab were calculated.

Keywords: Surface free energy, vibrational entropy, vibrational frequency, slab model, crystal surface

1. Introduction

The *surface free energy* [$\gamma_{(hkl)}^{T}$ (J/m^2)] of a (hkl) crystal face is the specific Helmholtz free energy needed for the creation of a crystal surface at the temperature T of interest. Such thermodynamic quantity is fundamental for the determination of:

(i) the most stable surface, that is the surface with the lowest surface free energy;

(ii) the equilibrium morphology of a crystal, by applying the Gibbs–Wulff's theorem;[1]

(iii) the probability of occurrence of *classical* nucleation with respect to the *non-classical* one, where an amorphous precursor phase is expected to form.[2-5] Indeed, by inserting the $\gamma_{(hkl)}^{T}$ values into the equations of the classical nucleation theory, the thermodynamic barrier to be overcome for stabilizing the critical nuclei can be calculated. If this classical barrier results to be extremely high, a non-classical nucleation could be hypothesized, which should require a fairly lower, or even null, activation energy for the formation of an amorphous phase with respect to a crystalline one.

Usually, $\gamma_{(hkl)}^{T}$ is calculated by comparing the free energy of the bulk crystal (F_{bulk}) with that of a two-dimensional periodic structure (slab model) of given thickness (F_{slab}), cut parallel to the *hkl* crystal plane of interest (i.e., Rubbo et al.[6]): $\gamma_{(hkl)}^{T} = \left(F_{slab} - F_{bulk}\right)/A = \Delta F / A$, where A is the area of the surface. This kind of model can provide a faithful description of the ideal surface, provided that the convergence of geometry, energy, and electronic properties, with the increasing number of atomic layers forming the slab, is checked (in the following, this point will be referred to as the *criterion of convergence*). In order to perform such a calculation, two different schemes can be envisaged to deal with a slab model (i.e., Dovesi et al.[7]):

(i) by imposing 2D periodic boundary conditions. The slab model is really two-dimensional, with a 2D unit cell.

(ii) By forcing a 3D periodicity (3D slab model). The three-dimensional system consists of an array of slabs of given thickness along one direction, separated by *vacuum zones*. The vacuum zones must be *thick* enough in order to reduce to zero the fictitious interactions between contiguous slabs.

However, the application of the 2D or 3D slab model should give the same result.

Unfortunately, by using this calculation strategy, the excess thermodynamic quantities like $\Delta F = F_{slab} - F_{bulk}$ and $\Delta S = S_{slab} - S_{bulk}$ (excess entropy) are exclusively assigned to the crystal surface, as it is not possible to establish the contribution of the different layers forming the slab to

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these excess quantities, which are nothing else that the integrated values of unknown density functions (i.e., free-energy density) over the thickness of the slab.

The excess thermodynamic quantities $\Delta F = F_{slab} - F_{bulk}$ obviously arises as the consequence of the deviation of the free energy of the slab with respect to the corresponding bulk quantity; as such deviation is likely to be *produced* in the layers which are closer to the free surface, with respect to those more deeply buried in the slab, it may be interesting to analyze the contribution of the various layer to the excess quantity, as a function of the distance of each of them from the surface. To this end, in this work we propose a new calculation strategy to estimate the vibrational contribution of each layer or atom forming the slab to $\Delta F^{vib} = F_{slab}^{vib} - F_{bulk}^{vib}$ (i.e., the excess vibrational free energy of a slab due to the existence of the surface) and, as a consequence, to determine how the vibrational free energy density varies within the slab. Furthermore, as will be discussed below, by means of this new calculation methodology it is possible to estimate the vibrational contribution to $\gamma_{(hkl)}^{T}$ without calculating the vibrational contribution of the bulk, F_{bulk}^{vib}. In other words, we can estimate how the surface energy changes with temperature by taking into account the slab entropic contribution only, which is due to the vibrational motion of the atoms in the slab (vibrational entropy).
Finally, we extend the model to the calculation of the vibrational contribution to the free energy of the interface between (i) two identical crystals in twinning relationship, and (ii) two different crystals in epitaxial relationship.

Our model presupposes the ability to calculate the frequencies of the vibrational modes of a slab, whose values enter into the thermodynamic equations to compute the vibrational energy, entropy and free energy. Nowadays, this can be done by using several codes developed for performing empirical (i.e., GULP,[8] TINKER[9]), semi-empirical (i.e., MOPAC[10]) and *ab initio* quantum-mechanical (i.e., ABINIT,[11,12] CASTEP,[13] CRYSTAL,[14] Quantum ESPRESSO,[15] VASP[16]) calculations on crystalline materials. Our model can be implemented in all of these codes, but at the time being it was implemented in a homemade program (SLAB), which is designed to read the output files of the CRYSTAL[14] and GULP[8] simulation codes and it is freely available to the web page http://mabruno.weebly.com/download.

The paper is structured as follow: (i) a short review of the calculation methodology and equations used to determine the vibrational free energy of a crystal face; (ii) description of our new model to analyze the vibrational free energy of a slab and calculate the vibrational contribution to the surface free energy; (iii) application of our model to the (100) slab of LiF and (10.4) slab of calcite ($CaCO_3$), and discussion of the results; (iv) main conclusions and perspectives.

2. The surface free energy of a crystal face

The free energy of a crystal face, $\gamma_{(hkl)}^{T}$, at the temperature T is composed by the following terms:[17]

$$\gamma_{(hkl)}^{T} = \gamma_{(hkl)}^{0K} + \gamma_{(hkl)}^{T,vib} + \gamma_{(hkl)}^{T,config} \quad (1)$$

where: (i) $\gamma_{(hkl)}^{0K}$ is the surface energy at $T = 0K$ (the specific work needed for creating and relaxing a crystal face at 0K and without considering vibrational zero point effects); (ii) $\gamma_{(hkl)}^{T,vib}$ is the vibrational (thermal) contribution (the specific internal vibrational energy and vibrational entropy at the temperature T, including the zero point energy contribution); (iii) $\gamma_{(hkl)}^{T,config}$ is the specific surface configurational entropy, which is related to the number of possible configurations of the surface, and it is given by the Boltzmann entropy formula, $\gamma_{(hkl)}^{T,config} = -\left(k_B T \ln W\right)/A$, being W the number of the surface configurations and k_B is the Boltzmann constant.

According to the CRYSTAL strategy,[14] $\gamma_{(hkl)}^{0K}$ is calculated by means of the following relation:[7]

$$\gamma_{(hkl)}^{0K} = \lim_{n\to\infty} E_s(n) = \lim_{n\to\infty} \frac{E(n)_{slab} - nE_{bulk}}{2A} \quad (2)$$

where A is the area of the primitive unit cell of the surface, n is the number of layers in the slab, $E(n)_{slab}$ is the energy of a n-layer slab and E_{bulk} is the energy of a formula unit in a bulky crystal; the factor 2 in the denominator accounts for the upper and lower surfaces of the slab. $E_s(n)$ is thus the energy per unit area required to form the surface from the bulk. As more layers are added in the calculation ($n \to \infty$), $E_s(n)$ will converge to the surface energy per unit area ($\gamma_{(hkl)}^{0K}$).

Instead, according to the standard two-region strategy employed by GULP,[8] $\gamma_{(hkl)}^{0K}$ is evaluated from the energy of the surface block of the crystal (region 1, U_s) and the energy of a portion of bulk crystal (U_b) containing the same number of atoms as the surface block:[18]

$$\gamma_{(hkl)}^{0K} = \frac{U_s - U_b}{A} \quad (3)$$

where A is the surface area.

The thermal contribution $\gamma_{(hkl)}^{T,vib}$ can be evaluated by calculating, both at *ab initio* and empirical level, the frequencies of the vibrational modes for the bulk crystal and the slab limited by the faces of interest.[6] This allows to calculate the vibrational partition function for the slab and the bulk crystal, $Z_{slab/bulk}^{vib} = \prod_i \prod_k e^{-\frac{h\nu_{ik}}{2k_B T}} \Big/ \left(1 - e^{-\frac{h\nu_{ik}}{k_B T}} \right)$ and, as a consequence, the vibrational energy ($E_{slab/bulk}^{vib}$) and entropy ($S_{slab/bulk}^{vib}$) of the slab and bulk crystal:

$$E_{slab/bulk}^{vib} = \xi_k k_B T^2 \left(\frac{\partial}{\partial T} \ln Z_{slab/bulk}^{vib} \right) = \sum_i \sum_k \xi_k \left\{ \frac{1}{2} h\nu_{ik} + \frac{h\nu_{ik}}{e^{\left(\frac{h\nu_{ik}}{k_B T}\right)} - 1} \right\} \quad (4)$$

$$S_{slab/bulk}^{vib} = \xi_k k_B \left(T \frac{\partial}{\partial T} \ln Z_{slab/bulk}^{vib} + \ln Z_{slab/bulk}^{vib} \right) = \sum_i \sum_k \xi_k \left\{ -k_B \ln\left[1 - e^{\left(-\frac{h\nu_{ik}}{k_B T}\right)} \right] + \frac{h\nu_{ik}}{T\left[e^{\left(\frac{h\nu_{ik}}{k_B T}\right)} - 1 \right]} \right\} \quad (5)$$

where h is the Planck constant, ν_{ik} is the frequency of the ith vibrational mode at the kth point in the Brillouin zone, in the slab or bulk crystal and ξ_k represents the weight of that particular **k** point, such that the sum of all weights is equal to one (as an example, if the number of **k** points is 10, then ξ_k is equal to 1/10). Then, the vibrational contribution to the surface free energy is obtained through the relation:

$$\gamma_{(hkl)}^{T,vib} = \frac{E_{slab}^{vib} - E_{bulk}^{vib}}{A} - T\frac{S_{slab}^{vib} - S_{bulk}^{vib}}{A} = \frac{F_{slab}^{vib} - F_{bulk}^{vib}}{A} \quad (6)$$

where $F_{slab/bulk}^{vib} = E_{slab/bulk}^{vib} - TS_{slab/bulk}^{vib}$ is the vibrational free energy of the slab and bulk crystal. It is to be noted that by using such a strategy it is not possible to establish the contribution to $\gamma_{(hkl)}^{T,vib}$ of each layer forming the slab or, in other words, it is not possible to determine how the vibrational free energy density varies within the slab. For obtaining this information it is necessary to face the problem from another point of view, as explained in the following section.

3. A new strategy to analyze the thermodynamic properties of a slab

For a slab composed by $j = 1, \ldots, n$ atoms there are *3n-3* vibrational modes with frequency v_{ik} ($i = 1, \ldots, 3n-3$ and $k = 1, \ldots, m$, being *m* the number of **k** points in the Brillouin zone; this number is obviously virtually infinite; however, by using the supercell strategy as it is implemented in CRYSTAL,[14] the Brillouin zone is sampled at a finite number of **k** points). The vibrational modes are described by eigenvectors of the mass weighted Hessian matrix (normal modes). Then, the contribution of each atom forming the slab to the ith vibrational mode can be evaluated by designing a weight function taking into account the vibrational amplitudes of the atoms involved in the vibrational mode (these are related to the components of the eigenvector representing the normal mode, referring to the displacements of any given atom along the three orthogonal directions of the reference frame). It is licit to build such a weight function, as the vibrational amplitudes of the atoms are expected to be modified by the presence of the surface. Otherwise stated, when a surface is present, there could be vibrational modes mainly involving atoms close to the surface, being small or negligible the contribution from farther atoms. Therefore, by identifying with $\mathbf{a}_{jkv_{ik}}$ the eigenvector associated to the jth atom and v_{ik}^{th} frequency at the kth point in the Brillouin zone, we are able to define the weight function:

$$p_{jkv_{ik}} = \frac{\left|\mathbf{a}_{jkv_{ik}}\right|^2}{\sum_j \left|\mathbf{a}_{jkv_{ik}}\right|^2} \quad (7)$$

for which holds the relation $\sum_j p_{jkv_{ik}} = 1$. Then, by multiplying eqs 4 and 5 with eq 7, we can calculate the contribution of the jth atom (E_j^{vib}, S_j^{vib} and F_j^{vib}) to $E_{slab}^{vib}, S_{slab}^{vib}$ and F_{slab}^{vib}:

$$E_j^{vib} = \sum_i \sum_k p_{jkv_{ik}} \xi_k \left\{ \frac{1}{2} h v_{ik} + \frac{h v_{ik}}{e^{\left(\frac{h v_{ik}}{k_B T}\right)} - 1} \right\} \quad (8)$$

$$S_j^{vib} = \sum_i \sum_k p_{jk v_{ik}} \xi_k \left\{ -k \ln\left[1 - e^{\left(-\frac{h v_{ik}}{k_B T}\right)} \right] + \frac{h v_{ik}}{T\left[e^{\left(\frac{h v_{ik}}{k_B T}\right)} - 1 \right]} \right\} \quad (9)$$

$$F_j^{vib} = E_j^{vib} - TS_j^{vib} \quad (10)$$

Finally, as a consequence of the definition of the weight function:

(i) $E_{slab}^{vib} = \sum_j E_j^{vib}$, $S_{slab}^{vib} = \sum_j S_j^{vib}$ and $F_{slab}^{vib} = \sum_j F_j^{vib}$;

(ii) if the E_{slab}^{vib} (J/mol), S_{slab}^{vib} (J/mol/K) and F_{slab}^{vib} (J/mol) values are normalized to a mole of the number of formula units forming the slab, then also the E_j^{vib}, S_j^{vib} and F_j^{vib} values are normalized to the same amount of matter.

It is now possible to calculate the contribution given by a selected group of atoms to E_{slab}^{vib} and S_{slab}^{vib} by consistently adding the different terms of E_j^{vib} and S_j^{vib}. As an example, since we are interested to analyze the thermodynamic properties of a slab, we can evaluate the contribution of each layer of the slab by grouping together the atoms belonging to the same d_{hkl} layer (interplanar distance: the distance between adjacent hkl planes) and adding their E_j^{vib} and S_j^{vib} values. In the following we reported the results of this analysis performed on the (i) 28-layer (100) slab of LiF and (ii)10-layer (10.4) slab of calcite ($CaCO_3$) by using the program SLAB.

3.1. Calculation of the vibrational contribution to the surface free energy ($\gamma_{(hkl)}^{T,vib}$)

In this section we report the relations to be used for the calculation of the vibrational contribution to the surface free energy ($\gamma_{(hkl)}^{T,vib}$; J/m^2) for (i) center-symmetric slabs in which all the atoms and the two surfaces delimiting them are allowed to relax (i.e., CRYSTAL strategy) and (ii) not center-symmetric slabs where the atoms of the region 1 only are allowed to move, and only one surface relaxes (i.e., GULP strategy).

Concerning a center-symmetric slab formed by $l = 1, \ldots, p, p+1, \ldots, 2p$ layers (Fig. 1a), $\gamma_{(hkl)}^{T,vib}$ is calculated by using the following equation:

$$\gamma_{(hkl)}^{T,vib} = \left(\sum_{l=1}^{2p} f_l^{vib} - 2pf_p^{vib} \right) pd_{hkl} \quad (11)$$

where f_l^{vib} is the density of the vibrational free energy (J/m^3) of the lth layer and f_p^{vib} is the density of the vibrational free energy of the layer p at the center of the slab; in this relation, as well as in the following ones, we must consider a vibrational free energy density, which is multiplied by a length (the thickness of half slab, pd_{hkl}) for obtaining the surface energy expressed in J/m^2. When the slab is thick enough to satisfy the criterion of convergence, that is when the bulk-like properties are reproduced at the center of the slab, the quantity $2pf_p^{vib}$ converges to the term F_{bulk}^{vib} of the eq 6 and the resulting $\gamma_{(hkl)}^{T,vib}$ value is a correct estimate of the surface vibrational contribution.

As concerns a non center-symmetric slab (Fig. 1b), the surface vibrational contribution is evaluated with the equation:

$$\gamma_{(hkl)}^{T,vib} = \left(\sum_{l=1}^{2p} f_l^{vib} - 2pf_p^{vib} \right) 2pd_{hkl} \quad (12)$$

where f_p^{vib} is the vibrational free energy density of the layer p, the layer at the center of the region 1. Even in this case, when the thicknesses of the regions 1 and 2 satisfy the criterion of convergence, $2pf_p^{vib}$ converges to the term F_{bulk}^{vib} of the eq 6 and a realistic estimate of $\gamma_{(hkl)}^{T,vib}$ is obtained.

FIGURE 1

3.2. Calculation of the vibrational contribution to the interface free energy

Our model can be also employed to analyze how the thermodynamic functions vary within (i) a twinned slab or (ii) a slab composed by two different phases (multi-phase slab) in epitaxial relationship. The calculation strategy is always the same: the E_j^{vib}, S_j^{vib} and F_j^{vib} terms are calculated by inserting into the eqs 8-10 the vibrational frequencies of an optimized twinned/multi-phase slab.

A twinned slab, made by slabs 1 and 2 (Fig. 2a), can be generated in the following way:

(i)   slab 1 of a given thickness is made by cutting the bulk structure parallel to the *hk.l* twin plane (the original composition plane, OCP) of interest;

(ii) slab 2 is made by applying the appropriate twin law to the atomic coordinates of slab 1.

A fundamental thermodynamic quantity related to a twinned slab is the *twinning free energy* (γ_{TE}^{T}; J/m²), which is excess free energy required to form a unit area of the twin boundary interface at the temperature T of interest. By analogy with the surface free energy, γ_{TE}^{T} can be written as the sum of three terms:

$$\gamma_{TE}^{T} = \gamma_{TE}^{0K} + \gamma_{TE}^{T,vib} + \gamma_{TE}^{T,config} \quad (13)$$

γ_{TE}^{0K} is the excess potential energy at 0K required to form a unit area of the twin boundary interface and reads:

$$\gamma_{TE}^{0K} = \frac{E_T - E_{NT}}{A} \quad (14)$$

where E_T and E_{NT} are the potential energies of the optimized twinned and not-twinned slabs, respectively; further details on the calculation of this quantity are reported in the paper by Bruno et al. (2010). $\gamma_{TE}^{T,config}$ is the specific configurational entropy of the interface.

$\gamma_{TE}^{T,vib}$ is the vibrational contribution of the twin boundary interface and, for a twinned slab composed by l =1, …, 2p layers (Fig. 2a), it is determined with the relation:

$$\gamma_{TE}^{T,vib} = \left(\sum_{l=p/2}^{3p/2} f_l^{vib} - p f_{p/2}^{vib} \right) p d_{hkl} \quad (15)$$

where $f_{p/2}^{vib} \equiv f_{3p/2}^{vib}$ is the vibrational free energy density of the layer *p/2≡3p/2*. As in the previous cases, when the thicknesses of the slabs 1 and 2 satisfy the criterion of convergence, $p f_{p/2}^{vib} \equiv p f_{3p/2}^{vib}$ converges to F_{bulk}^{vib}.

As concerns a slab composed by two phases in epitaxial relationship (A and B, Fig. 2b), a fundamental thermodynamic quantity to evaluate is the *interface free energy*, γ_{int}^{T} (J/m²), the excess free energy required to form a unit area of the interface between the phases A and B. Similarly to

γ_{TE}^{T}, γ_{int}^{T} is the sum of the potential (γ_{int}^{0K}), configurational ($\gamma_{int}^{T,config}$) and vibrational contributions($\gamma_{int}^{T,vib}$). γ_{int}^{0K} is calculated by using the relation:

$$\gamma_{int}^{0K} = \frac{E_{AB} - E_A - E_B}{A} \quad (16)$$

where E_{AB}, E_A and E_B are the potential energies of the optimized multi-phase slab, slab of the only phase A and slab of the only phase B, respectively. Instead, by considering a multi-phase slab composed by $l = 1, \ldots, 2p$ layers of the phase A and $s = 1, \ldots, 2t$ layers of the phase B, $\gamma_{int}^{T,vib}$ is calculated by means of the following equation:

$$\gamma_{int}^{T,vib} = \left(\sum_{l=p}^{2p} f_l^{vib} - p f_p^{vib} \right) p d_{hkl}^A + \left(\sum_{s=1}^{t} f_s^{vib} - t f_t^{vib} \right) t d_{hkl}^B \quad (17)$$

where f_p^{vib} and f_t^{vib} are the vibrational free energy densities of the layers p and t, placed at the center of the phases A and B, respectively. If the thicknesses of the phases A and B satisfy the criterion of convergence, then $p f_p^{vib}$ and $t f_t^{vib}$ converge to F_{bulk}^{vib} of the phases A and B, respectively.

FIGURE 2

4. Application of the model to the (100) slab of LiF

The (100) slab of LiF was recently studied by our research group.[6] We performed quantum-mechanical *ab initio* calculations on 4- 8- 12- 16- 20- and 28-layer slabs, in order to determine the surface structure and the surface free energy of the (100) face. The slab geometry optimization and the calculation of the vibrational frequencies were performed using the CRYSTAL06 software for quantum-mechanical ab initio calculations,[14] which implements the Hartree-Fock and Kohn-Sham self consistent field (SCF) method for the study of periodic systems.[19] For a detailed analysis of the (100) surface structure and slab vibrational modes see the paper by Rubbo et al.,[6] whereas the computational details concerning the slab geometry optimization and the calculation of the slab frequencies, are reported in the Electronic Supplementary Information (ESI).

In this work the vibrational energy, entropy and free energy of the optimized 28-layer (100) slab, and the contributions of each atom (Li or F) and layer forming the slab were calculated at the temperature T = 298.15 K. The slab is composed by 28 layers and 56 atoms (a LiF unit per layer) related by an inversion center. Then, the thermodynamic analysis will take into account only the symmetrically independent layers (l =1, …, 14, where l = 1 is the surface layer) and atoms (j = 1, …, 28; where the atoms 1 and 2 are in the layer l =1).

In Fig. 3 the vibrational contribution of the layers (E_l^{vib}, S_l^{vib} and F_l^{vib}) is plotted; the numerical values are listed in Table S1 and S2 (ESI). By analyzing Fig. 3, one observes an abrupt increase of E_l^{vib} moving from the surface toward the center of the slab. In order to give an idea, E_1^{vib} = 17107.9 and E_{14}^{vib} = 17672.9 J/mol. Instead, S_l^{vib} shows an opposite behavior, it decreases from the surface (S_1^{vib} =55,0 J/mol K) to the center of the slab (S_{14}^{vib} =43.3J/mol K). As a consequence, F_l^{vib} shows an analogous behavior to E_l^{vib}: F_1^{vib} = 696.3 and F_{14}^{vib} = 4769.1 J/mol.

In order to understand the contribution of the atomic species to the free energy of each layer forming the slab, in Fig. 4 we have reported the values of the free energy of the layers (F_l^{vib}) along with those of the Li and F atoms (see Table S1, ESI). It is interesting to observe that:

(i)   the highest contribution to the slab free energy is given by the Li atoms. Indeed, at the center of the slab the free energy of Li and F is 4615.3 and 153.8 J/mol, respectively. This means that the ~97% of the slab free energy at the center of the slab is due to Li.

(ii)   The free energy of F is negative in the layers 1-4, whereas that of Li is always positive.

Finally, by applying eq 11, we also calculated the vibrational contribution to the surface free energy: $\gamma_{(100)}^{298K,vib}$ = -0.01 J/m^2. Then, by adding this value to the surface energy at 0K ($\gamma_{(100)}^{0K}$ = 0.338 J/m^2) calculated by Rubbo et al.[6] for the 28-layer slab, we obtained the surface free energy of the (100) face at 298.15K, $\gamma_{(100)}^{298K}$ = 0.328 J/m^2. Here, it is important to stress that this values was obtained considering a 28-layer slab, the value of $\gamma_{(100)}^{298K}$ we estimated does not satisfy the criterion of convergence on the thickness of the slab. In order to have a more reliable estimate of $\gamma_{(100)}^{298K}$, a calculations on a thicker (100) slab should be performed.

FIGURES 3 and 4

5. Application of the model to the (10.4) slab of calcite

The vibrational frequencies of an optimized (10.4) slab of calcite were calculated at empirical level by using the calcite force field developed by Rohl et al.[20] and the version 4.0 of the General Utility Lattice Program (GULP) simulation code[8] 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 surface energy values at $T = 0$K of the $\{10\overline{1}4\}$ and $\{01\overline{1}2\}$ faces obtained from *ab initio* calculations at DFT (Density Functional Theory; B3LYP[21] and PBE[22] Hamiltonians) level,[23-25] as well as the experimental observations of the surface relaxation of the $\{10\overline{1}4\}$ form.[20] Furthermore, a fairly good agreement exists between the twinning energies of the four twin laws of calcite calculated with the Rohl potential[26] and those determined at DFT level.[27]

We performed the calculations at $T = 300$K by considering a (10.4) slab formed by $l = 1, ..., 10$ layers and $j = 1, ..., 300$ atoms (with six $CaCO_3$ units per layer) in both region 1 and 2. The frequencies of the vibrational modes of the region 1 of the (10.4) slab were calculated by considering 30 **k** points. Therefore, the vibrational energy, entropy and free energy that we computed concerns exclusively the region 1 of the (10.4) slab. We are acknowledge that this is not a sufficient number of **k** points for reaching convergence on the thermodynamical properties of the slab, but our purpose in this case is just to show the ability of the model to discriminate between the different contributions of the layers to the thermodynamic properties of the slab; in order to obtain more reliable estimates of the thermodynamic properties, a greater number of **k** points should be used.

As in the case of LiF, in Fig. 5 we reported the vibrational contribution of the layers (E_l^{vib}, S_l^{vib} and F_l^{vib}); the numerical values are listed in Table S3 and S4 (ESI). We observe an analogous behavior to LiF concerning S_l^{vib}, whereas F_l^{vib} and E_l^{vib} show a very different trend. Indeed, a damped oscillation of the F_l^{vib} and E_l^{vib} values is observed, with the highest amplitude of the oscillation at the slab surface.

Another evident feature of the curves reported in Fig. 5 is the strong variation of the E_l^{vib}, S_l^{vib} and F_l^{vib} values associated to the layer 10 with respect to the ones relative to the previous layers. This is due to the calculus methodology implemented in the GULP program, where the vibrational frequencies of the atoms placed to the bottom of the region 1 are strongly affected by the rigid behavior of the region 2. That is, the environment surrounding the atoms at the bottom of the region

1 is different with respect to that of the atoms located far away the interface between region 1 and region 2 of the slab. For this reason the frequencies of the atoms located at the bottom of the region 1 are affected by errors and, as a consequence, the vibrational thermodynamic properties of the layer 10 deviate from the correct trend.

Also for calcite, in order to understand the contribution of the atomic species to the free energy of each layer forming the (10.4) slab, in Fig. 6 we have reported the values of the free energy of the layers (F_l^{vib}) along with those of the Ca, C and O atoms (see Table S3, ESI). We observe that:

(i)   the highest contribution to the slab free energy is given by the C and O atoms. At the center of the slab (layer 6) the free energy of Ca, C and O is 1316.8, 102571.1 and 108761.4 J/mol, respectively. This means that the ~99% of the free energy at the center of the slab is due to the CO_3 groups.

(ii)   The free energy of Ca is negative only in the layers 1.

By applying eq 12, we calculated the vibrational contribution to the surface free energy: $\gamma_{(10.4)}^{300K,vib}$ = -0.250 J/m^2. Then, by adding this value to the surface energy at 0K ($\gamma_{(100)}^{0K}$ = 0.534 J/m^2) calculated by using eq 3, we obtained the surface free energy of the (10.4) face at 300K, $\gamma_{(10.4)}^{300K}$ = 0.284 J/m^2. As for the LiF case, it is important to stress that this values was obtained considering a 10-layer slab. Then, the value of $\gamma_{(10.4)}^{300K}$ we estimated does not satisfy the criterion of convergence on the thickness of the slab and number of **k** points. Indeed, a more reliable estimates of $\gamma_{(10.4)}^{300K}$ was very recently obtained by Bruno et al.,[17] which gave 0.464±0.018 J/m^2.

FIGURES 5 and 6

6. Conclusions

In this paper we describe a new calculation methodology for determining the vibrational contribution of each layer or atom forming the slab (i.e., how the vibrational free energy density varies within the slab). Now, by means of this new calculation methodology, it becomes possible to estimate the vibrational contribution to the surface free energy of a crystal face ($\gamma_{(hkl)}^{T}$) without calculating the vibrational contribution of the bulk: we estimate how the surface energy changes with temperature by only taking into account the entropic contribution due to the vibrational motion of atoms in the slab. Finally, our model is extended to the calculation of the vibrational contribution

to the free energy of the interface between (ii) two identical crystals in twinning relationship and (ii) two different crystals in epitaxial relationship.

Our model uses the frequencies of the vibrational modes of a slab, which can be determined by means of several free or commercial codes developed for performing calculations on crystalline materials, and it is based on the construction of a weight function taking into account how the vibrational amplitude of the atoms involved in the vibrational mode is modified by the presence of the surface. Indeed, when a surface is present, there are vibrational modes in which atoms near the surface take part to a higher degree than atoms far away from the surface. Our calculation strategy was implemented in a homemade program (SLAB), which is designed to read the output files of the CRYSTAL[14] and GULP[8] simulation codes. However, in principle our model can be implemented in all of the codes developed for performing semi-empirical, empirical and *ab initio* quantum-mechanical calculations on crystalline materials.

In order to test our model, we applied it to the following systems: (i) 28-layer (100) slab of LiF and (ii) 10-layer (10.4) slab of calcite ($CaCO_3$). In both cases, the vibrational energy, vibrational entropy and vibrational free energy of the optimized slab, and the contribution to these quantities of each atom and layer forming the slab were calculated. Since we are only interested to show how our model works, in this paper we have only reported the calculations at room temperature ($T = 298.15$ K and $T = 300$ K, for LiF and $CaCO_3$, respectively), we did not analyze how the temperature affects the thermodynamic properties of the slab; this analysis will be object of study in a future work.

Our model could be also employed to analyze how the vibrational free energy density is modified when a point defect (i.e., a Schottky or Frenkel defects) is introduced into the bulk structure of a crystal. Indeed, it is sufficient to calculate the vibrational frequencies of the "defective" crystal and apply our model for obtaining the vibrational free energy of each atom: the vibrational free energy of the atoms close to the point defect should be somewhat different with respect to that of the atoms far away from the point defect. Finally, our model could be used to study a defective surface (i.e., a stepped slab), by determining how the vibrational free energy density varies from the stepped surface to the bulk.

Electronic Supplementary Information (ESI) Available. CRYSTAL computational details concerning the slab geometry optimization and the calculation of the slab frequencies of LiF; Table S1: vibrational energy, entropy and free energy at T = 298.15 K of Li and F atoms forming the (100) slab of LiF; Table S2: vibrational energy, entropy and free energy at T = 298.15 K of the layers forming the (100) slab of LiF; Table S3: vibrational energy, entropy and free energy at T = 300 K of Ca, C and O atoms forming the (10.4) slab of calcite; Table S4: vibrational energy, entropy and free energy at T = 300 K of the layers forming the (10.4) slab of calcite.

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Figure captions

Figure 1. Schematic representation of a center-symmetric (a) and not center-symmetric slab (b); diagrams showing a qualitative trend of the vibrational free energy of the layer $l = 1, \dots, 2p$ for the two cases, are also reported. Symmetrically equivalent layers are represented by equal colors. In (a), where the slab preserves the inversion center, the layers 1, 2, …, p are equivalent to the layers 2p, 2p-1, …, p+1, respectively. In (b), where the inversion center is not preserved, no equivalent layers exist in region 1.

Figure 2. Schematic representation of a twinned (a) and multi-phase slab in epitaxial relationship (b); diagrams showing a qualitative trend of the vibrational free energy of the layers for the two cases, are also reported. Symmetrically equivalent layers are represented by equal colors.

Figure 3. Vibrational energy (E_l^{vib}), entropy (S_l^{vib}) and free energy (F_l^{vib}) of the layers $l = 1, \dots, 14$ of the (100) slab of LiF at $T = 298.15$ K. Each layer is formed by a LiF unit.

Figure 4. Vibrational free energy of the layers $l = 1, \dots, 14$ of the (100) slab of LiF at $T = 298.15$ K. The vibrational free energy of the atoms (Li and F) forming the slab is also reported.

Figure 5. Vibrational energy (E_l^{vib}), entropy (S_l^{vib}) and free energy (F_l^{vib}) of the layers $l = 1, \dots, 10$ of the (10.4) slab of calcite at $T = 300$ K. Each layer is formed by six $CaCO_3$ units.

Figure 6. Vibrational free energy of the layers $l = 1, \dots, 10$ of the (10.4) slab of calcite at $T = 300$ K. The vibrational free energy of the atoms (Ca, C and O) forming the slab is also reported.

Graphical abstract
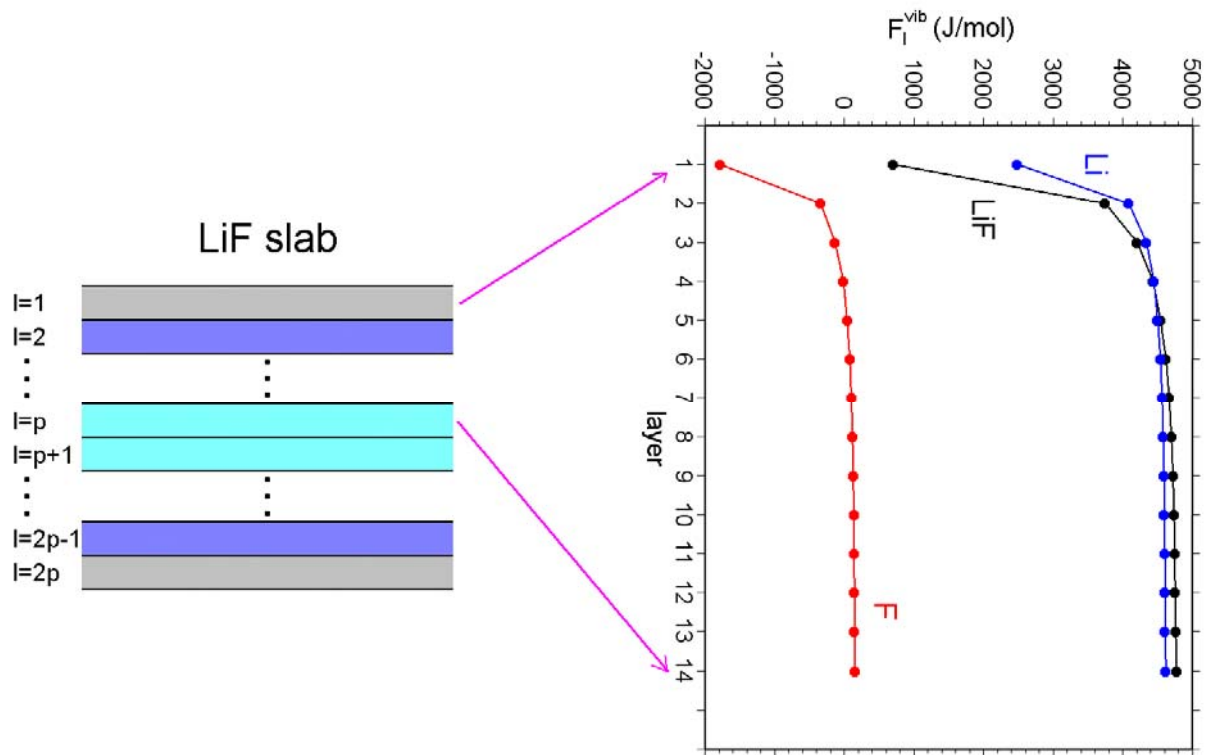
We developed a new calculation strategy for determining the vibrational contribution of each layer or atom forming a slab. By means of this new calculation methodology, it is now possible to estimate how the surface free energy of a crystal face changes with temperature by only taking into account the entropic contribution due to the vibrational motion of atoms in the slab.