

Free Energies of Molecular Crystal Surfaces by Computer Simulation: Application to Tetrathiophene

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The crystallization of molecular compounds is a critical step for several chemical processes and technologies, ranging from pharmaceuticals to advanced materials. Take, for example, "organic electronics":¹ solid-state organization of the molecules, crystal morphology and orientation with respect to a possible substrate are crucial factors for the performance of a material. Knowledge of the energetics of crystal interfaces can be a useful complement to structural information^{2,3} from scanning probe microscopies or grazing-angle diffraction to gain a better understanding of growth and polymorphism in crystals and thin films. Experimental determination of the free energies γ_i of crystal surfaces (the i subscript denotes a lattice plane) is possible in a few cases, but it is highly nontrivial.⁴ More often, only the ratios γ_i/γ_j can be inferred from the crystal shape by the Wulff construction,⁵ assuming that this is an equilibrium one and does not depend instead on the kinetics of crystal growth.⁶ Here we present a general method to obtain the surface free energies of a molecular crystal by computation. We then illustrate it by an application to tetrathiophene, a system of great current interest for organic electronics whose crystals and thin films can be grown by sublimation or molecular beam deposition.^{7–9}

Ionic, semiconducting, and metallic solids display surface relaxation and reconstructions, which can be quite important from both structural and energetic points of view. These being "hard" materials, their surfaces are relatively static, and entropic phenomena are expected to be unimportant, at least around room temperature. Thus, computational approaches¹⁰ which obtain surface energies by simple minimization seem to be adequate in these cases. The situation is reversed for molecular crystals. Their surfaces usually undergo very small relaxation with respect to the bulk.^{2,3} However, these are "soft" materials with molecular interaction energies of the order of a few $k_B T$ ($T \cong 300$ K). Large-amplitude molecular motions about the "unrelaxed" average positions may become possible on going from the constraining environment of the bulk (where both attractive and repulsive forces are at work¹¹) to the surface. Thus one expects significant entropic contributions to the surface free energy, even at room temperature. These considerations motivated the present study.

We set up a simulation box as shown in Figure 1. This depicts a slab of material with 2D periodic boundary conditions, parallel to the crystallographic plane of interest. The slab comprises a few crystal unit cells along both the orthogonal and periodic directions, which are also several times larger than the cutoff distance for nonbonded interactions (12 Å). The slab is divided in two regions, A and B , which are to be separated to expose two crystal surfaces. In turn, each region is divided in two parts: in one of them the atoms are allowed to move by molecular dynamics (MD), whereas in the other they are fixed at their bulk equilibrium positions to simulate the crystal underneath. All simulations were performed with the TINKER molecular modeling package.¹² The Supporting Information contains further details on the force field and the simulation methods.

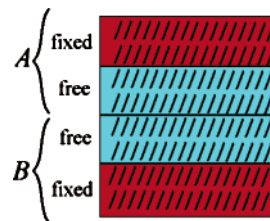


Figure 1. General scheme of a simulation box. Each oblique segment represents a tetrathiophene molecule.

To evaluate the reversible work needed to cleave the crystalline slab, we write a generalized Hamiltonian of the system as a function of a coupling parameter λ and a positive integer n :

$$H_n(\lambda) = (T_A + V_A) + (T_B + V_B) + \lambda^n V_{AB} \quad (1)$$

where T_A , T_B and V_A , V_B are the intraregion kinetic and potential energies. V_{AB} is the inter-region potential energy, which consists of a sum over all nonbonded interactions (Lennard-Jones and electrostatic) across the A/B interface. The free energy difference between the bulk ($\lambda = 1$) and the free surfaces ($\lambda = 0$) can then be obtained by the thermodynamic integration method:¹³

$$\Delta A = \int_0^1 \left\langle \frac{\partial H_n}{\partial \lambda} \right\rangle_\lambda d\lambda = - \int_0^1 n \lambda^{n-1} \langle V_{AB} \rangle_\lambda d\lambda \quad (2)$$

The specific surface free energy γ_i is given by:

$$\gamma_i = \frac{\Delta A}{2S} \quad (3)$$

where S is the cross-section area of the simulation box. Division by 2 follows from the fact that two identical surfaces are created upon cleaving the crystal.

The integrand in eq 2 is the average of the *full* interaction energy, calculated over an ensemble of configurations consistent with a *rescaled* interaction between the regions. We compute it by a series of MD simulations at decreasing λ 's. The value of $\langle V_{AB} \rangle_\lambda$ at arbitrary λ can be obtained by interpolation through 4–5 neighboring points. Finally the integral can be evaluated by standard numerical methods.¹⁴ The result does not depend on the details of the interpolation and integration schemes. Instead, the choice of the n parameter turns out to be critical.

According to our experience, $\langle V_{AB} \rangle_\lambda$ may diverge to infinity as $\lambda \rightarrow 0$, especially at high T . The reason is that when $\lambda \cong 0$ a molecule at the surface of region A may overlap with another molecule from region B , due to their thermal motion. Whenever this happens, their *unscaled* Lennard-Jones repulsion becomes practically infinite. This divergence makes it difficult to evaluate eq 2 accurately when $n = 1, 2$. However it is sufficient to set $n \geq 3$ to have a well-behaved integrand: the λ^{n-1} prefactor damps the divergence of $\langle V_{AB} \rangle_\lambda$ as λ

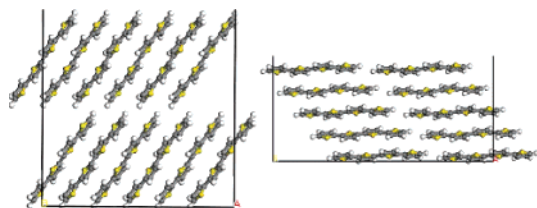


Figure 2. Two surfaces of the HT tetrathiophene crystal: left side (001) surface, right side (101) surface.

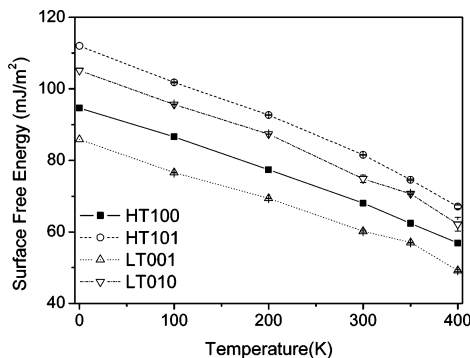


Figure 3. Free energies as a function of temperature for four selected surfaces of the two polymorphs of tetrathiophene.

→ 0. We have checked that the free energy integrals with $n = 3$ and $n = 4$ are virtually identical.

Tetrathiophene crystallizes in two different forms, namely the so-called LT (Low Temperature) and the HT (High Temperature) polymorphs.^{7,8} We have simulated four different surfaces, two for each polymorph. These are the LT-(001) and HT-(100) surfaces, with the molecules standing approximately perpendicularly on the surfaces, and the LT-(010) and HT-(101) surfaces, with the molecules lying flat on the surfaces. The two HT surfaces are shown in Figure 2. For each surface, the temperature dependence of the free energy was obtained by simulations at 100, 200, 300, 350, and 400 K. Also, the values at 0 K were computed as differences of the energies of the two end states (bulk and cleaved crystal), which were obtained in turn by molecular mechanics minimization. The final results are plotted in Figure 3.

The calculated surface free energies are of the order of 0.1 J m^{-2} . This is fairly typical for organic materials.^{10b,c} The near-linear temperature dependence of the surface free energies is readily interpreted according to the textbook relation $\Delta A = \Delta U - T\Delta S$, where the energy and entropy differences are roughly constant over the investigated temperature range. The slope ($\cong -0.1 \text{ mJ m}^{-2} \text{ K}^{-1}$) is roughly twice larger than in ionic metal oxides.¹⁵ Since the latter have surface energies of 1 J m^{-2} or more, the relative contribution of the $T\Delta S$ term is in fact much more important in the present case. This confirms our qualitative expectations.

In principle, surface entropy may be identified with positional, orientational, or conformational disorder at the surface. An exhaustive analysis of this problem lies outside the scope of this communication. Here we simply compare the distribution of the inter-ring torsion angles within the bulk and the surfaces. These torsions are exactly or nearly trans-planar in the HT and LT crystals, respectively. Figure 4 contains a graph for the HT-(101) surface at 300 K, showing that the distribution of the dihedral angles is broader than in the bulk. We even find some surface dihedral angles in a cis conformation ($\cong 10\%$). This conformational disorder increases with temperature. The LT-(010) surface has the same behavior, while the conformational difference between the surface and the bulk is less evident for the surfaces with “standing” molecules, HT-(100) and LT-(001). Thus, the similar slope of the plots is somewhat

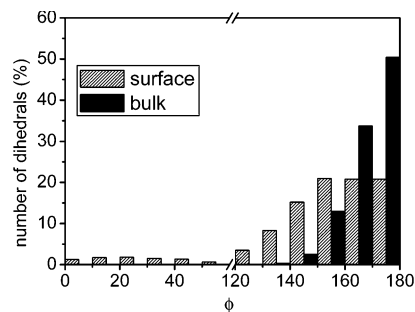


Figure 4. Angular distributions for the S-C-C-S torsions, from the simulations of the HT-(101) surface at 300 K. We only consider the two terminal bonds of each molecule. The surface histogram includes only the molecules in the outermost layer.

nontrivial and unexpected, in the light of these results and the different molecular arrangements at the four surfaces (see again Figure 2). Further work needs to be done to clarify this point.

In summary, we have presented a general computational scheme to obtain the surface free energy of molecular crystals. Our first application has shown that thermal effects can be quite significant. We are now planning further applications of the method. For example, entropic phenomena are expected to be even more important in multicomponent systems, such as cocrystals. The method can also be adapted to study the thermodynamics of nanosized crystals, since their free energy can be approximated as the sum of bulk and surface terms.^{9b,16}

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Supporting Information Available: Details of the simulation methods; Tinker-style force field parameter file for tetrathiophene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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