

Simulation of the Surface Properties of Molecular Crystals

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Abstract

The surface structure of molecular crystals is of interest for several applications, such as the crystallization of pharmaceutical compounds or the properties of thin films for organic electronics. Unlike inorganic solids, such as ionic or semiconductor crystals, molecular solids generally show no reconstructions and little relaxation at the surface. However, molecular motions at the surface and within the bulk of the crystals may be significantly different in this case. Computer simulation by Molecular Dynamics (MD) is a useful complement to experimental investigations by methods such as AFM (Atomic Force Microscopy), which can hardly detect these effects. Our group has applied it to the investigation of molecular crystal surfaces. We have also implemented a method for the calculation of surface free energies, which are not readily measured experimentally. The method, which employs the technique of “thermodynamic integration”, requires significant computer resources.

La struttura superficiale dei solidi molecolari è di interesse per diverse applicazioni, quali la cristallizzazione di sostanze farmacologicamente attive o le proprietà di film sottili di materiali per l'elettronica organica. A differenza dei solidi inorganici, quali ad esempio i cristalli ionici o di semiconduttori, i solidi molecolari generalmente non mostrano significative ricostruzioni o rilassamenti superficiali. Tuttavia, in questo caso i moti delle molecole alla superficie possono differire significativamente rispetto all'interno del cristallo. La simulazione al computer mediante tecniche di Dinamica Molecolare (MD) è un valido complemento all'indagine sperimentali con metodi quali l'AFM (Microscopia di Forza Atomica), che non riescono facilmente a rilevare questi effetti. Il nostro gruppo l'ha applicata all'indagine delle superfici dei cristalli molecolari. Abbiamo anche implementato un metodo per il calcolo delle energie libere di formazione delle superfici, che non sono facilmente accessibili sperimentalmente. Il metodo, che utilizza la tecnica della “integrazione termodinamica”, richiede significative risorse di calcolo.

Keywords: molecular dynamics (MD); molecular crystals; surfaces and interfaces; free energy calculations.

Introduction

The surface structure of molecular crystals affects their growth (hence their size and shape) as well as several of their final properties (solubility or optical properties, for example). There are many cases of practical interest, such as pharmaceuticals or organic semiconductors, where one would like to characterize precisely their surface in order to optimize their application. For example, in the case of materials for optoelectronic applications (organic LEDs, transistors, photovoltaic cells, etc.) one is often working with thin films (a few nm's thick) deposited on a suitable substrate. Clearly, the thinner the film, the larger will be the contribution of the surfaces to its overall properties. It has been shown that the performance of these devices depends critically on the degree of crystallinity, the formation of a specific crystal polymorph as well the orientation of the crystals/molecules with respect to the substrate.

Grazing angle X-ray or neutron diffraction and Atomic Force Microscopy (AFM) are powerful experimental methods for the study of the surface structure of these and other materials. The studies conducted so far have shown that organic molecular crystals, from relatively simple systems such as the acene series (condensed aromatic hydrocarbons) up to the complex case of proteins, do not show the reconstruction or relaxation phenomena often observed in inorganic solids (covalent, metallic or ionic). It is generally observed that the overall periodicity and topography of their surface closely reflect the structure of the bulk of the crystal.[1] However, these techniques generally lack atomic-level resolution: for example, the contact area in AFM microscopy is determined by the curvature radius of the AFM tip, which is typically of 15-30 nm. Atomic-level details can be easily obtained by computer simulation, which thus represents an ideal complement to these experimental techniques. Our group has used the Molecular Dynamics (MD) method to investigate the structure and energetics of molecular crystal surfaces. In the following sections we provide a brief account of our recent activity in this field.

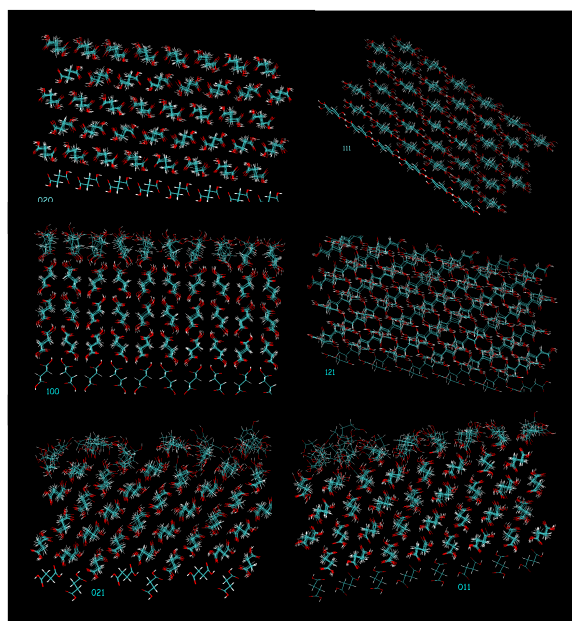


Figure 1: snapshots from MD simulations of different surfaces of the β polymorph of succinic acid. The exposed crystal surface corresponds to the uppermost molecular layer in each picture. The coordinates of the molecules in the lowermost layer have been fixed at the bulk equilibrium positions, to simulate the crystal underneath the surface. The pictures have been obtained using VMD.[6]

Disorder at the surface of molecular crystals: empirical evidence from simulation

The MD method consists in solving Newton's classical equations of motion for all the atoms within a suitably chosen sample of material.[2] The forces between the atoms arise from bonding as well as non-bonding interactions, which are represented by simple functions of the atoms' coordinates parametrized by comparison with experimental data and/or *ab initio* electronic structure calculations. The initial atomic coordinates for the simulations are taken from experimental X-ray structures of the crystals, which are then "truncated" along specific crystallographic planes in order to expose different surfaces. Currently, our typical simulations follow the motion of $\approx 10^4$ atoms for $\approx 10^1$ ns. The atomic

coordinates generated during these trajectories are saved on disk and analyzed afterward to extract relevant properties. The simulations are done using the TINKER molecular modelling package.[3]

Figure 1 shows six instantaneous snapshots from MD simulations at room temperature (300 K) of selected low-energy surfaces of the so-called β form of succinic acid ($\text{HOOC-CH}_2\text{-CH}_2\text{-COOH}$). This is a thoroughly studied model system, representative also of other hydrogen-bonded crystals. The pictures show that while the molecules at some surfaces retain a degree of order comparable to those in the bulk [(020), (111) and (121) surfaces], the molecules at other surfaces are somewhat more disordered [(100), (021) and (011) surfaces]. When present, this disorder can involve displacements of the molecular centres-of-mass or large-amplitude motions of the molecular backbone (positional and conformational disorder). Even in these cases, however, we do not observe a true “melting” of the outermost molecular layer, and the molecules in the second layer immediately underneath already seem to have a bulk-like crystalline order (apart from small-amplitude oscillations about the equilibrium positions).

These observations, along with similar ones on the crystals of tetrathiophene — a completely different system whose intermolecular interactions are dominated by relatively aspecific van der Waals interactions as opposed to strong and directional electrostatic forces — are in qualitative agreement with the general diffraction and AFM results discussed in the Introduction. When observed at relatively low resolution (above 5-10 Å, say), the surfaces closely reflect the bulk structure. However, the simulations unveil also the possibility of atomic- or molecular-level disorder (i.e., entropy). This is not altogether unreasonable, considering that the typical interaction energies between two molecules are only a few times larger than the room-temperature “thermal energy” ($RT=2.49$ kJ/mol at $T=300\text{K}$). In the case of ionic or covalent solids, where the atoms are chemically bonded together and are therefore subject to much stronger forces, comparable disordering phenomena are generally observable only at much higher temperatures ($T>1000$ K, as a rough estimate).

Disorder at the surface of molecular crystals: free energy calculations

In addition to characterizing the structure of the crystal-vacuum interfaces, it is also of interest to quantify their energetic content. The specific surface energy represents the total amount of work which must be performed in order to create a specific *unit* surface (it is measured in J/m^2), by “cleaving reversibly” an infinite crystal along a given

crystallographic plane. This is an important quantity which determines, for example, the equilibrium shape of a crystal. However there is no simple, direct and generally applicable way to measure it experimentally. Its calculation by molecular modelling thus represents an attractive alternative avenue.

Roughly speaking, the “standard” method for the evaluation of the surface energies[4] consists in computing the energy of a infinite crystal and of a two-dimensional slab of material of finite thickness, and normalizing their difference by the area of the surface of the slab. The energies of the crystal and of the slab are obtained by minimizing their energy with respect to all the atomic coordinates. This method, which is relatively simple and fast, accounts for surface relaxation phenomena. However, because of its static nature, it does not include the effect of the room-temperature molecular motions which were described above. Thus it is expected to be valid only at relatively low temperatures. In order to have a general solution to the problem, it is necessary to have a method which includes entropic phenomena. In other words, we need to compute a surface *free* energy (remember the textbook relation $\Delta A = \Delta U - T\Delta S$, where ΔA , ΔU and ΔS are the free energy, the internal energy and the entropy changes, while T is the absolute temperature). We have proposed a solution to this problem,[5] exploiting the “thermodynamic integration method”. [2] This has often been used in other contexts to compute the free energy difference between two arbitrary states of a system (the binding of different pharmaceutical molecules to the active site of a protein, for example). In essence, the method requires several MD simulations of two contacting “half-crystals”.

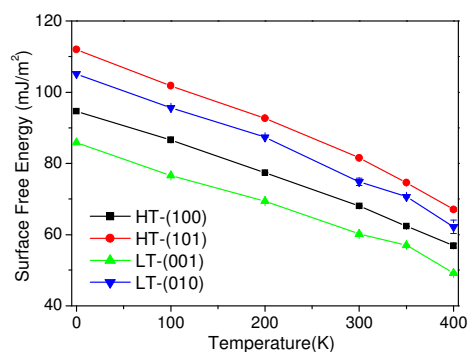


Figure 2: Temperature dependence of the surface free energies, for two different surfaces of each of the two known polymorphs of tetrathiophene. Redrawn after ref.[5].

The interaction between them is gradually switched off by a factor λ , thus passing from the original bulk-like situation (when $\lambda=1$) to two fully separated, non-interacting crystal surfaces (when $\lambda=0$). Integration of average interaction energy between the two half-crystals with respect to the λ parameter produces the required surface free energy.

The results from the first application of the method to selected surfaces of two crystalline forms of tetrathiophene (the so-called LT and HT polymorphs) are shown in Figure 2.[5] The points at 0 K actually correspond to static calculations by the method of Rohl and Gay.[4] The Figure clearly demonstrates that, as the temperature rises, there is an almost linear decrease of the surface free energy. This corresponds to the previously recalled relation $\Delta A = \Delta U - T\Delta S$, where ΔU is the intercept with the y axis and the negative slope corresponds to $-\Delta S$. Thus there is a positive increase in the entropy upon forming the surface, in agreement with our qualitative expectations (the surfaces are more disordered than the bulk). The correction due to this term is quite significant even at room temperature, and corresponds to about 30% of the surface energy at 0 K. Note however that all the curves have similar slopes, so that this correction does not produce an inversion in their relative values, at least in this case.

Finally, we briefly discuss a strictly computational aspect of the problem. Although each of our individual free energy calculations can be run on a single-processor workstation, they still require very significant computing power. In order to obtain a single point of those shown in Figure 2, it was necessary to perform 15 individual MD simulations at different values of the λ parameter. Each of these lasted 0.15 ns, in order to accumulate reliable averages. Thus, all together, the production of Figure 2 required about 50 ns of simulations on systems of several thousand atoms. We have estimated that these would have taken 4-5 years, if they had been run sequentially on one single-processor computer.

Conclusions

The MD simulation of the surfaces of molecular crystals is a very useful complement to experimental investigations of their structure and energetics. The first applications have shown that these can provide both qualitative insights and detailed quantitative information. The calculations of the free energies of the surfaces of succinic acid shown in Figure 1 is currently in progress, and they will represent an important test of the generality and robustness of our approach. If these are successful, we will move on to more complex applications, which will certainly require considerable computing power.

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