Surface Incorporation of a growth unit on the (020) crystal face of alpha-Glycine

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Summary

In order to estimate the absolute perpendicular growth rate of a crystal surface, we need to estimate the free energy barrier for the incorporation and removal of growth units. In this work, an all-atom molecular dynamics with biased umbrella sampling and WHAM was used to calculate the potential of mean force (PMF) as a function of the perpendicular distance between the growth unit and the surface of one of the crystal faces of alpha-glycine. From the PMF curve, the surface incorporation/disincorporation energy (binding energy) was estimated.

Background

Surface incorporation of solute molecules on a growing crystal terrace from the solvent of crystallization (or vacuum in the case of vapor growth) is the first step for the growth of the particular crystal face. Crystal morphology prediction is of tremendous significance to save hundreds of expensive experiments. Relevant mechanistic understanding of crystal growth is essential for both academic and industrial purposes. The determination of absolute growth rates of crystal faces is of immense interest but there is no directed effort in this direction to the best of knowledge. Valuable information can be extracted about surface integration and kink incorporation by free energy calculations and molecular modeling.

Simulation Methods

An all-atom Generalized AMBER force field with Particle-Mesh Ewald summations was chosen in the GROMACS package as alpha-glycine has multiple atom types and strong long-range electrostatics behavior. The 020 crystal surface was created having 228 molecules (2280 atoms) (reading a pdb unit cell file and converting it to 6x2x6 supercell in GROMACS) and a surface glycine molecule was marked and its distances recorded with the center of the slab as reference. The other molecules in the crystal lattice were position restrained.

11 independent MD simulations with umbrella sampling (force constant of 2500 KJ/nm^2) using the NPT ensemble and Berendson thermostat (with temperature coupling) were carried out after initial independent equilibration runs at 300K. We carried out long production runs (500000) steps with different restraint force targeting to a different y each time. The trajectories were saved and read in using Python. We recorded the probability of reaction coordinate y, using histogram counts and the histograms were stitched together using the Weighted Histogram Analysis Method (iterative analysis) discussed in class. The histograms were reweighted and we plotted the PMF as a function of the reaction coordinate y and we estimated the binding energy (or the incorporation energy) from the free energy curve.

Results and Interpretation

The histograms from each simulation are shown in Figure 1. The center of the slab (reference point) is 1.1 nm away from the molecule that is leaving the surface. The restraining harmonic potential had to be modified using trial and error until a good overlap was seen in the histograms. The combined histograms showing the total number of counts before applying the WHAM is shown in Figure 2. Figure 3 shows the potential of mean force along the reaction co-ordinate y from which we can calculate the free energy of the barrier to detach or the binding energy.

WHAM calculations using the method outlined in the course notes converged to within a low tolerance after around 25000 iterations. The second (smaller) hump in Figure 2 and Figure 3 away from the surface is just due to the restraining force (the molecule is no longer under the attractive force of the crystal surface but is not flown away in vacuum because of the restraining potential)

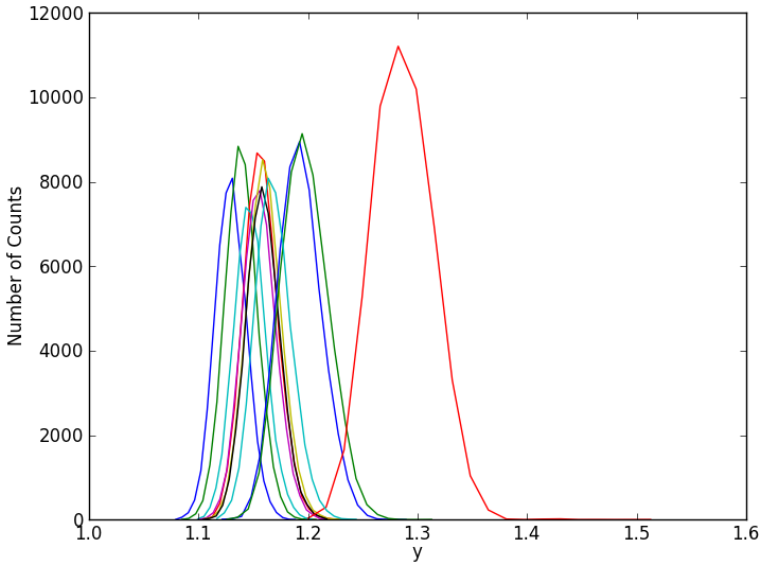

Fig 1: Histograms of counts recorded from 11 independent simulations.

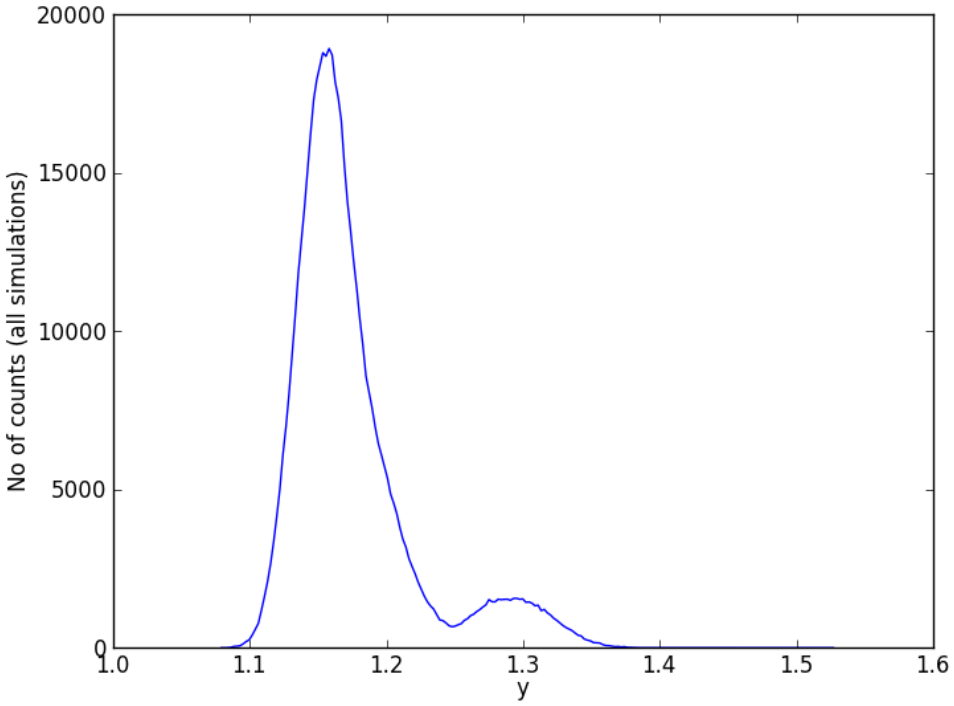

Fig 2 : A combined histogram of total counts of reaction coordinate y

The bold vertical line in Figure 3 represents the energy barrier for the detachment of a glycine molecule from the surface. The magnitude of this barrier is about 7 kcal/mol, or about 12 kT. There are no estimates for this value in the literature, so further detailed calculations have to be made about the absolute growth rates of crystal surfaces and then compared to experimental values to observe the validity of this method.

Discussion and Improvements: This is just the first step for computing the absolute growth rates for crystal faces. Apart from the center of mass distance y, orientation is another obvious reaction co-ordinate. So, ultimately, one has to do a multidimensional potential of mean force surface calculation to get a more accurate estimate of the free energy barrier. A molecular vector needs to be defined for that

purpose.

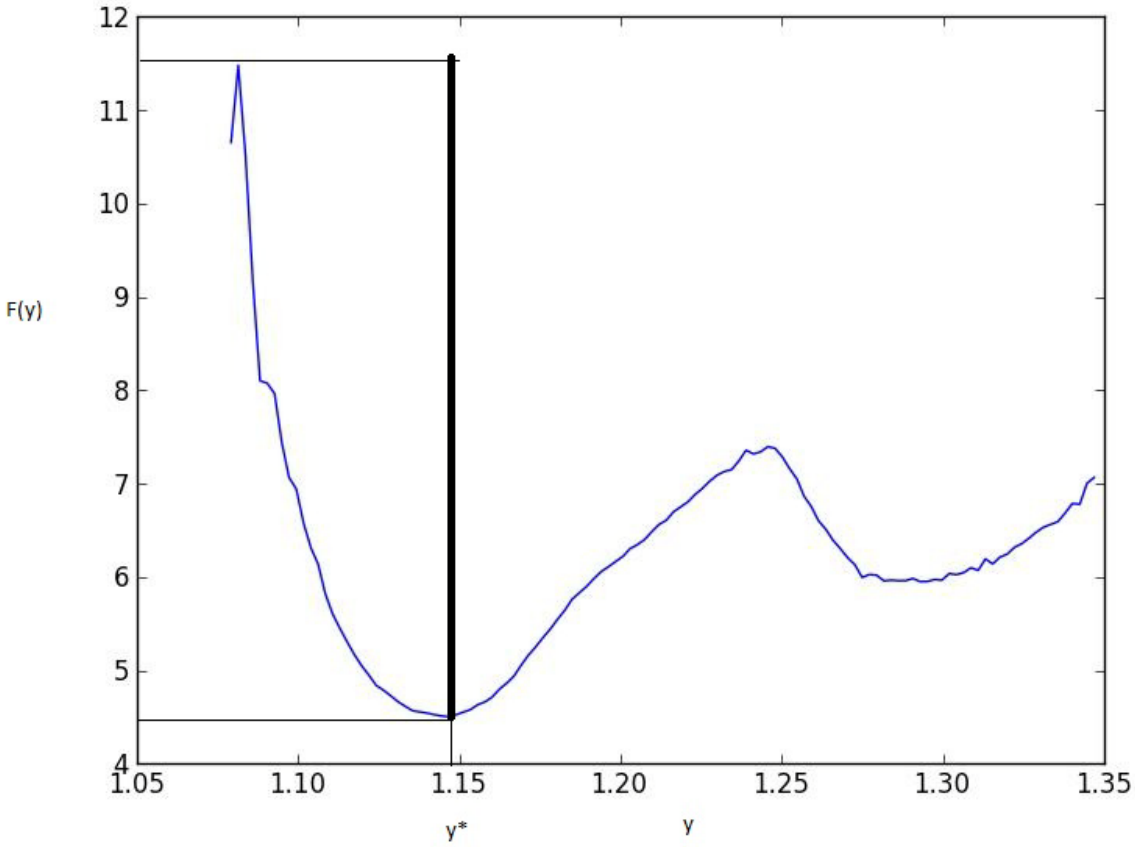

Fig 3 :The potential of mean force F(y) as a function of reaction coordinate y

Another important step extension would be to repeat the calculations for different possible sites on different crystal surfaces and also use an explicit solvent model.

Movie : 210dmovie3.avi

This movie shows the trajectory of disincorporation of a surface glycine molecule from the crystal terrace using biased umbrella sampling.

Source Code:

ZKuvadia.rar