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Molecular Modeling of Diffusion on a Crystalline PETN Surface

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Abstract

Surface diffusion on a PETN crystal was investigated by treating the surface diffusion as an activated process in the formalism of transition state theory. In particular, surface diffusion on the (110) and (101) facets, as well as diffusion between these facets, were considered. We successfully obtained the potential energy barriers required for PETN surface diffusion. Our results show that the (110) surface is more thermally active than the (101) surface and PETN molecules mainly diffuses from the (110) to (101) facet. These results are in good agreement with experimental observations and previous simulations.

Pentaerythritol tetranitrate (PETN) is one of the most powerful explosives in use today. At room temperature, PETN forms in a tetragonal space group $P\bar{4}2_1c$ with two molecules per unit cell.[1] Atomic force microscopy (AFM) has shown that PETN molecules are quite mobile on the crystal surface even at temperatures as low as 30 °C.[2] The morphology of a PETN crystal can change through two proposed mechanisms: surface diffusion and sublimation, both of which are believed to occur simutaneously. Burnham *et al.*[2] used AFM and thermogravimetric analysis (TGA) evaporation experiments for investigating the process of sublimation. However, no experimental observations of surface diffusion have been made to date. In this work, we investigate surface diffusion of a PETN molecule on two different PETN crystal facets using a molecular mechanics approach.

In this study, the potential energy of a PETN crystal is described by the coarse-grained model recently proposed by Gee *et al.*[3] In that model, each of the four NO_2 groups is combined into a "*B*"-bead and the remaining atoms are grouped into a central "*A*"-bead. The model includes only two interactions: the intramolecular *A–B* bond interaction in the harmonic form: $E_{bond}(r_{AB}) = K_{bond}(r_{AB} - b_{AB}^0)^2$, where $K_{bond} = 20.0$ kcal/mol·Å^{-2}, $b_{AB}^0 = 2.6$ Å and the *B–B* nonbond interaction in the 12-6 Lennard-Jones form: $E_{vdw}(r_{BB}) = D_{BB}[(\sigma_{BB}/r_{BB})^{12} - 2(\sigma_{BB}/r_{BB})^6]$, where $D_{BB} = 1.38$ kcal/mol and $\sigma_{BB} =$ 4.84 Å. The cutoff distance for the nonbond interaction is 15 Å, about two molecular layers. This model was shown to accurately predict the lattice constants, the sublimation energy, the pressure-volume behavior (up to P=10 GPa), and expressed the energetically most stable facets. To validate our simulation setup, we did a NVE -MD simulation in the 3D simulation box to calculate the sublimation energy of our PETN coarse grained model.

Our result in a 200 ns run is 34 kcal/mol which is in reasonably good agreement with the value in the original paper,[3] 36 kcal/mol.

Zepeda-Ruiz *et al.*[4] demonstrated that the PETN crystals primarily exposes the (110) and (101) facets. Based on the coarse-grained model, we eatablish a four-layer PETN surface structure that consists of (110) and (101) facets, where both facets are connected (see Fig. 1). For clarity, only the top layers of each of the facets are shown in Fig. 1. The thickness of the surface structure is larger than the cutoff distance. To investigate the energy required for the PETN molecule to diffuse on the surface of a PETN crystal by transition state theory, an adiabatic potential energy surface (PES) for PETN is constructed by grid sampling the total potential energy of the system. The added PETN molecule was tethered to the specified position by a harmonic potential, similarly the surface molecules were also attached to their respective lattice positions by a harmonic potential. The total potential energy was then minimized by the conjugate gradient method.[5] Fig. 2 shows the PES for both facets resulting from the regular surface arrangement of PETN crystal. The relative low-energy paths (i.e., the thermodynamically most probable paths) for surface diffusion on both the facets as well as the channel betwen the two facets can be easily observed on the PES. The diffusion paths on the (101) facet go along (010) direction, while the diffusion paths on the (110) facet go along (112) direction.

Transition state theory (TST) has been widely used to study diffusion events on solid state materials.[6] Knowledge of the TS and the energy minima yields the energy of activation for PETN surface diffusion on a PETN crystal. Mathematically, the TS is a first-order saddle point on the PES i.e. a stationary point where the Hessian matrix of

second derivatives of the potential energy has only one negative eigenvalue. Finding the TS is more challenging than finding minima because the reaction coordinate is generally unknown.

In this work, we have used a combination of the first and the second derivative methods to locate the TS.[7] Initially, the first derivative method by Elber and coworkers[8,9] was used to find the approximate reaction coordinate (and hence a good initial guess for the TS) connecting the local minima for the diffusion process on the PES. Next, starting with this initial guess, the second derivative method formulated by Baker[10] was used to locate the exact TS. Since the PETN molecule shows very small displacements during the TS search process, only a partial Hessian matrix that consisted of the coordinates of the molecules within 30 Å from the diffusing molecule is used in this search.[11] After locating the TS, the reaction coordinate was determined as the steepest descent path from the TS to the local minima on the PES in mass-weighted Cartesian coordinates.[12]

Our approach successfully located the TS and the reaction coordinates for surface diffusion. Fig. 3 shows representative reaction coordinates for diffusion paths on the (110) and (101) facets. Qualitatively similar results were obtained for all 18 diffusion paths studied on the (110) facet and the 2 diffusion paths on the (101) facet. On the (110) facet, a symmetric energy barrier is observed along with a relatively flat high energy plateau near the TS. On the (101) facet, the reaction coordinate is an “m-shape” pathway with two TS locations and an intermediate local minimum. Fig. 4 presents the diffusion pathway for the crossing between two facets. For the three separate paths studied, the energy surface near the TS is seen to be complex. Four TS are located and the energy

barriers are in good quantitative agreement with each other. Table 1 lists the computed activation energies obtained in this work.

Table 1 Comparison of potential energy barriers for surface diffusion obtained from PES for PETN, transition state theory and literature. The unit is kcal/mol.

	PES	TST	Literature
(110) facet	2	2.46	1.85[13]
(101) facet	8	10.58	None
(110) to (101) facet	8	5.35	None
(101) to (110) facet	16	15.53	None

The following conclusions can be drawn from the above values of the energy barriers: the surface diffusion rate on the (110) facet is much faster than that on the (101) facet, similarly diffusion of the molecule from the (110) to (101) facet is a more likely event than diffusion in the opposite direction. The latter conclusion is in agreement with the experimental observations and previous Monte Carlo simulations, in that the aspect ratio of the crystal increases with time and temperature.[4] Furthermore, the energy barriers for diffusion from one facet to another are significantly lower than the sublimation energy (~ 35 kcal/mol) which was calculated using the same coarse grained model. Qualitatively, this observation indicates that surface diffusion will also play a very important role in the morphology change of PETN molecule and should be considered in interpreting experimental data on coarsening of the PETN crystals. Our calculations have focused only on the potential energy change of the process; a more complete physical

description can be obtained in future by calculating the free energy change for PETN diffusion. Another interesting extension will be repeating the calculations with an atomistic model of PETN. This will likely lead to a highly accurate value of the energy barriers but will result in more than an order of magnitude increase in the computational time.

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Figure Caption

Fig 1 Top layer of the PETN surface structure. Left side is the (101) facet and right side is the (110) facet.

Fig 2 Potential energy surface for PETN. The unit of energy is kcal/mol.

Fig 3 Energy profile for surface diffusion on the (110) and (101) facets.

Fig 4 Energy profile for surface diffusion between the (110) and (101) facets.

Figure changes: A larger font should be used in all figures. Fig. 2 needs a energy label on the right-y axis.

Fig 1

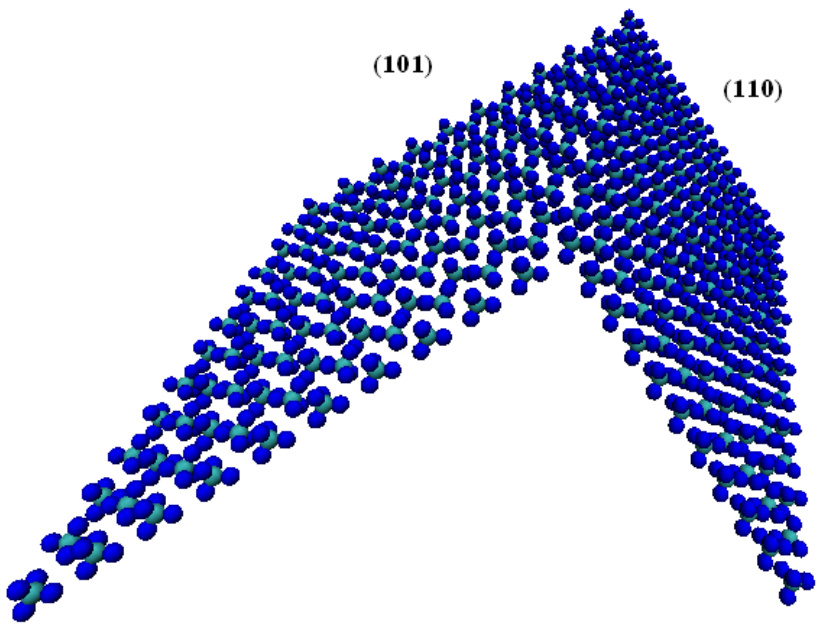


Fig 2

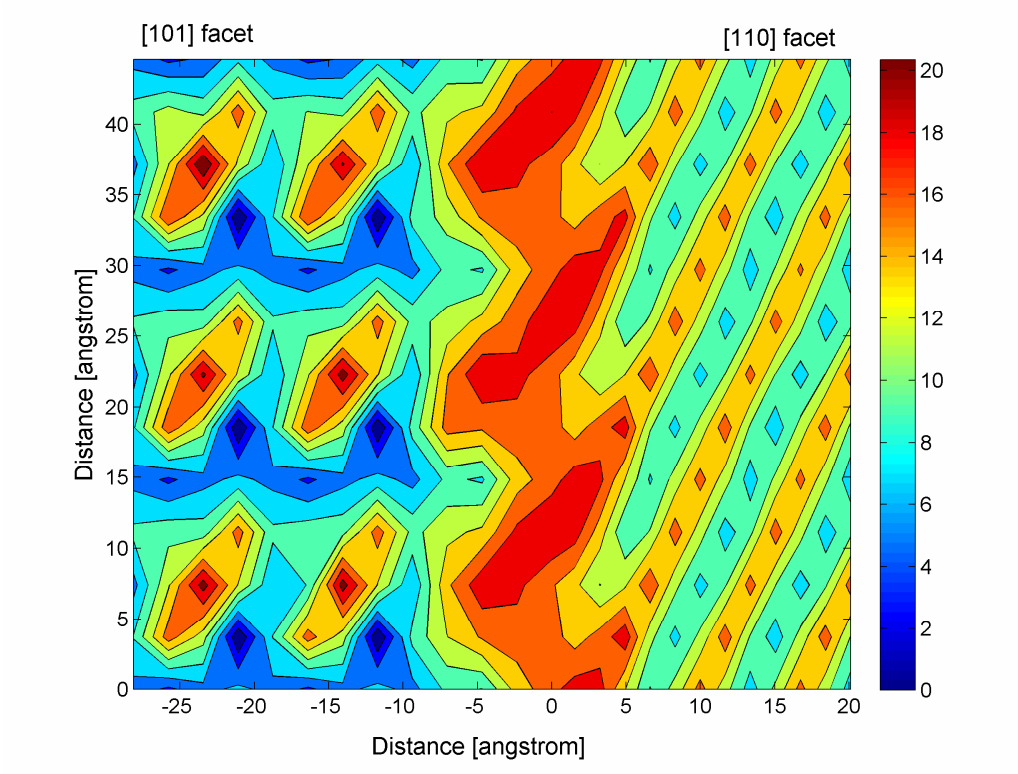

[101] facet
[110] facet
Distance [angstrom]
Distance [angstrom]
0
5
10
15
20
25
30
35
40
-25
-20
-15
-10
-5
0
5
10
15
20
0
2
4
6
8
10
12
14
16
18
20

Fig 3

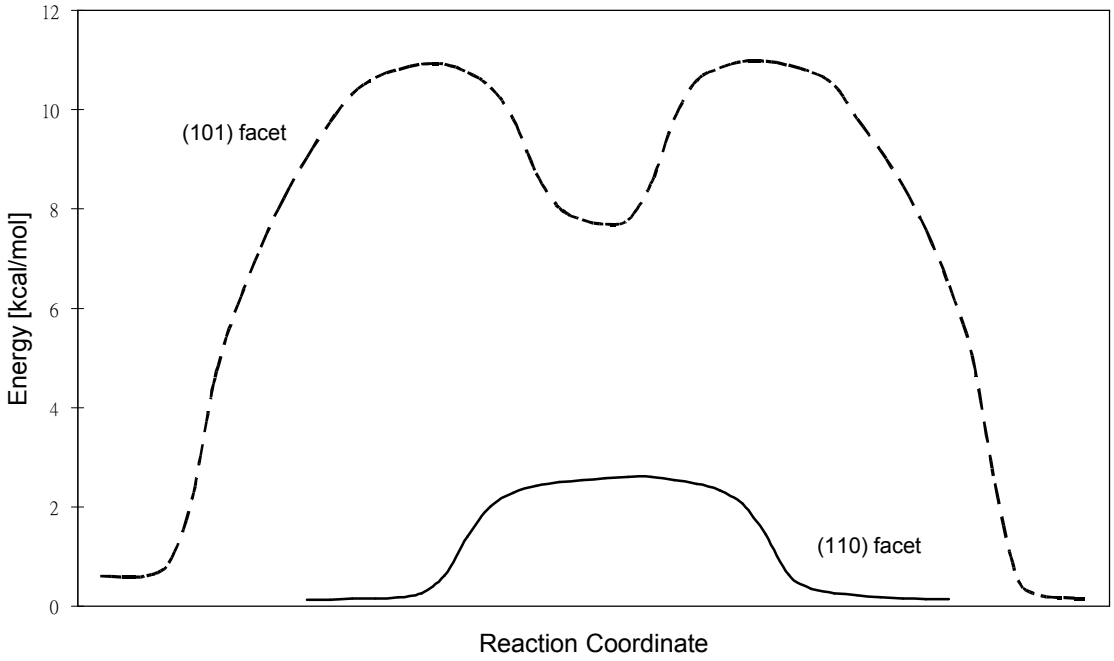
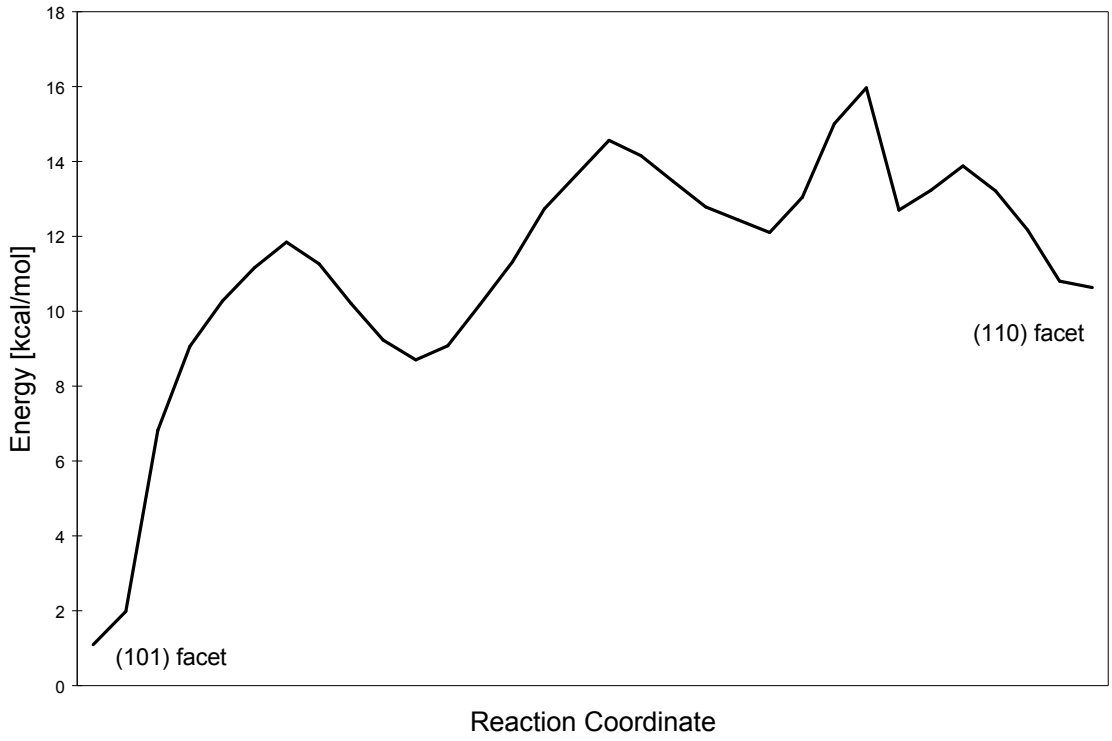

12
10
8
6
4
2
0
Energy [kcal/mol]
(101) facet
(110) facet
Reaction Coordinate

Fig 4


18
16
14
12
10
8
6
4
2
0
Energy [kcal/mol]
(101) facet
(110) facet
Reaction Coordinate

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