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# Epitaxy of folds in polyethylene crystals: molecular mechanics investigation

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Dedicated to the memory of John D. Hoffman, a good friend and colleague for many years.

## Abstract

In the prevailing thermodynamics associated with Gibbsian surface physics of a century ago, the surface of a crystal has an associated surface energy and surface stress that influences properties and morphology. This work uses molecular mechanics to investigate the surface energy and epitaxial packing of chain folds on the surfaces of adjacent crystals. It is shown that there are lower energy juxtapositions of the crystals resulting from energetically favorable epitaxial arrangements. These lower the excess surface energy with respect to the melt, but do not completely eliminate the discrepancy between the values of the surface energy from computational results and analysis of experimental data. The epitaxial arrangements are consistent with the experimentally observed rotational displacement of successive layers in multi-layer polyethylene crystals. Thus, they might influence the rotation of the successive layers resulting from screw dislocations.

*Keywords:* PE surface stress/energy; Epitaxy; Molecular mechanics

## 1. Introduction

In the prevailing thermodynamics associated with Gibbsian surface physics of a century ago, the surface of a crystalline material has an associated surface energy and stress. The former is the reversible work required to create a new unit area of surface by a process such as cleavage and the latter is the reversible work required to create a unit area of surface by deformation of a pre-existing surface [1]. Such parameters also can be defined for two solid phases that are separated by an interface such as the epitaxial ones that occur in polypropylene [2–4] and polyethylene [5,6]. Further, analyses of a quarter century ago of non-symmetric laminar materials showed that deformations of a curved and twisted nature can occur [7–9]. In light of the discussion above, it has long been recognized that the surface in polymers and alkanes can generate energy and stress which influences properties, structure and morphology. Examples are given by twisted lamellae, curved crystals, ridged lamellae, S-shaped crystals, anisotropic strain of unit cells, strain energy of the crystals, variation of cell dimensions with lamella thickness, melting temperature, specific heat, density, elastic properties and crystals with curved edges, among many others [10–31]. Related effects occur in other materials [32]. However, the concept had not been dealt with in a complete analytical manner for polymers until a more formal treatment was given [33]. Analysis yielded expressions for surface stress as a function of lamella thickness, elastic compliance of the crystal and strain of the unit cell dimensions with respect to those of an infinitely thick lamella. Use of the expression yielded surface stresses, which were qualitatively correct. That is, they corresponded to stresses that would increase the cell dimensions and were comparable to the excess energy of the surface with respect to the melt as is the case for other materials [32,33]. Except for these qualitative comparisons, there were only a few independent means of evaluating the results of the analysis at the time.

Therefore, computational modeling of the excess surface energies with respect to the melt and stresses were

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undertaken [34–36]. For *n*-paraffins, the unit cell dimensions and excess energy of the surface with respect to the melt agreed with the experimentally determined values. Further, the surface stresses also agreed reasonably with the values determined by the analysis mentioned above [33]. These results lent credence to the analysis and the modeling. For polyethylene, the unit cell dimensions also agreed well with the experimental values. However, neither the excess energy of the surface with respect to the melt nor the surface stresses agreed with the corresponding values determined by the analysis above [33]. The model took account of the fact that the surface stress for a free-standing crystal would not be the same as that between neighboring crystals [35,36]. That is, the folds extend above the crystal in a manner such that there would be periodic depressions among them. The consequences of a free-standing crystal would be missing favorable interactions with missing neighbors 'above' the surface. This would affect the magnitude of the energy and stress and would favor epitaxial interactions between the crystals. Such interactions might affect properties and might influence the rotation of successive layers resulting from screw dislocations in a multilayered crystal [37–39]. A possible explanation for the discrepancies noted above might be that the folds and stems of the polyethylene model were held fixed during the modeling. These represent somewhat unrealistic assumptions. Therefore, this note reports the results for the surface energy of allowing both the fold and stem conformations and orientations to change. Further, a newer force field with a substantially different functional form and method of parameterization is used.

## 2. Computational method

To evaluate the effects discussed above, the fold surface of a crystal with 24 stems and 12 folds was brought into opposition to another equivalent fold surface using Accelrys' Materials Studio [40]. Each fold and stem pair had 80 carbon atoms, with periodic boundary conditions along the *a* and *b* dimensions of the crystals. The initial dimensions of the orthorhombic unit cell and the setting angle of the stems were taken from previous experimental work on PE crystals [41], with $a = 7.388$ Å and $b = 4.929$ Å. The (110) fold was created by breaking one carbon–carbon bond at the center of the stems in an extended crystal of 80 carbon atoms and joining two neighboring stems with a carbon–carbon bond. A periodic supercell of 12 folds (24 stems) per crystal surface (with two opposing crystal surfaces) was created with a *Z* dimension sufficiently large enough (120 Å) that long range interactions from periodic images did not interact in the *Z* direction. This structure was minimized with Accelrys Discover using the Conjugate–Gradient method (Polak–Ribiere algorithm) with 10,000 maximum iterations and a convergence criterion of 10.0 kcal/mol/Å. The 'condensed-phase optimized molecular potentials for atomistic simulation studies' (COMPASS) force field was used [40]. The fold surface was normal to the axes of the stems, i.e. there was no staggering of folds within the fold surface. Also, the folds were initially 'knuckle-to-knuckle,' i.e. not shifted to fit the protrusions of one surface into the recesses of the other. The distance between the two surfaces was minimized, resulting in the closest contacts between hydrogen atoms of opposing surfaces with a separation distance of 2.36 Å. During minimization, the unit cell was allowed to change in size and shape. As a result, the dimensions after minimization were $a = 6.89$ and $b = 4.91$ Å while the shape remained orthorhombic.

During subsequent calculations, one crystal lamella surface was 'fixed', while the other was allowed to move in all directions, but was maintained parallel to the fixed surface. Operationally, the 'fixed' crystal was translated and/or rotated with respect to the unconstrained crystal, with the energy and geometric response of the unconstrained crystal being analyzed. Also, the initial perpendicular separation of the two surfaces was varied in order to discern changes in the interactions between the two surfaces with respect to the initial separation. The fold surfaces in opposition contained only folds, i.e. there were no chain ends in the opposing surfaces.

## 3. Results and discussion

Fig. 1 shows the PE crystal structure used in this work, presenting a view along the *Z*-axis and superimposing the (110) folds in the opposing surfaces (note the axis directions

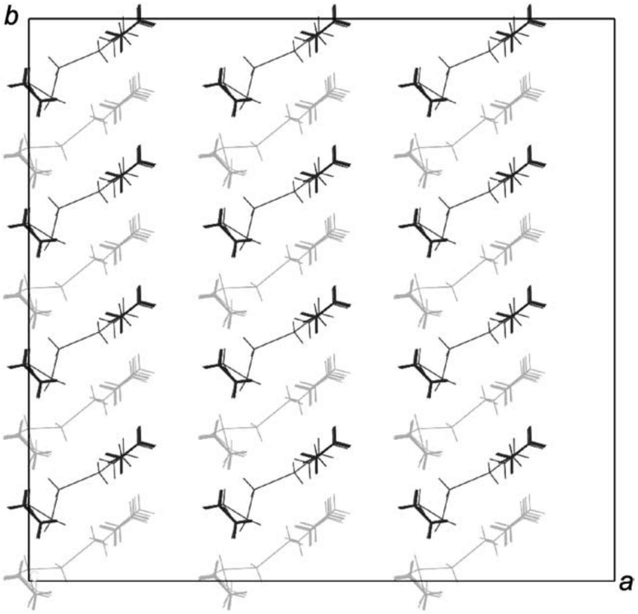

Fig. 1. The fold surface structure used for translation or rotation along the epitaxial surfaces. The view shown is down the chain principal axis, showing mirror image placement of the darker folds at the translation of 0.2 Å in the *a* direction and 2.5 Å in the *b* direction. Each carbon atom has two hydrogen atoms, which are not shown for clarity. The fixed crystal is rendered in grey while the other, translated crystal is rendered in black.

and that the origin is in bottom left corner). The image is three unit cells (∼20.7 Å) in the *a* direction and four (∼19.7 Å) in the *b* direction. The darker atoms represent one of the crystals that has been translated in the *a*, *b* directions with respect to the other crystal. This minor translation allows slight interdigitation and lowers the energy of the system. In contrast with previous work on the energetics of chain folding in PE crystals [42], the folding in this system occurs with a range of different sets of torsional angles and numbers of $CH_2$ groups incorporated in the fold. Although the folds in the two lamella were initially 'mirror images' of each other they relax independently, with non-bonded in-crystal interactions competing with non-bonded interactions between the opposing crystal surfaces. However, there is cooperativity of the stems within each crystal (e.g. all stems bend in the same direction if at all when displaced from equilibrium).

Fig. 2 shows the total potential energy of the simulation system as a function of translation in the *a* and *b* directions, during which one crystal is operationally translated with respect to the other crystal in the *a* and *b* directions while remaining fixed in the *Z* direction. The single point energy is calculated without allowing minimization of the simulation ensemble. The minimum used for subsequent calculations is marked with an x at a translation of 0.2 Å in the *a* direction and 2.5 Å in the *b* direction from the origin. There are also minima at translations of 0.2, 7.4; 7.1, 2.5; and 7.1, 7.4 Å in the *a*, *b* directions (respectively), with all the minima being equal in energy. The fact that the four minima (corresponding to translational symmetry across the four unit cells included in the translation grid) are identical in energy means that the principal axis in the *c* dimension of the crystal is the same as the *Z* dimension of the periodic cell. All of the minima corresponding to the translations in *a*, *b* mentioned above are of structures where the folds of opposing crystal surfaces are offset to allow minor interdigitation of the folds, as shown in Fig. 1.

To assess the notion of minor rotation in subsequent layers of epitaxially grown PE crystals, one crystal was rotated with respect to its original configuration and with respect to the other crystal, yielding the data shown in Fig. 3. The rotation of one crystal about its principal axis (central *c*-axis) with respect to the other crystal is plotted against the total potential energy of the system for the initial structure of 'knuckle-to-knuckle' placements of the fold surface (i.e. the 0° rotation energy is equal to the energy at the origin of Fig. 2), plotted as dots. The solid line is of the system rotated about the minimum of Fig. 2 (i.e. the 0° rotation energy is equal to the energy at the minima of Fig. 2 corresponding to a translation of 0.2 Å in the *a* direction and 2.5 Å in the *b* direction from the origin). The absolute value of total potential energy is not meaningful here; rather the changes in total potential energy as one crystal is rotated from zero degrees of rotation are significant. The important point to mention is that there is a significant decrease in the total potential energy between the translated sample and the original structure. However, although the translation reduces the total potential energy significantly, at the translation minimum a further reduction in the total potential energy is not possible without further

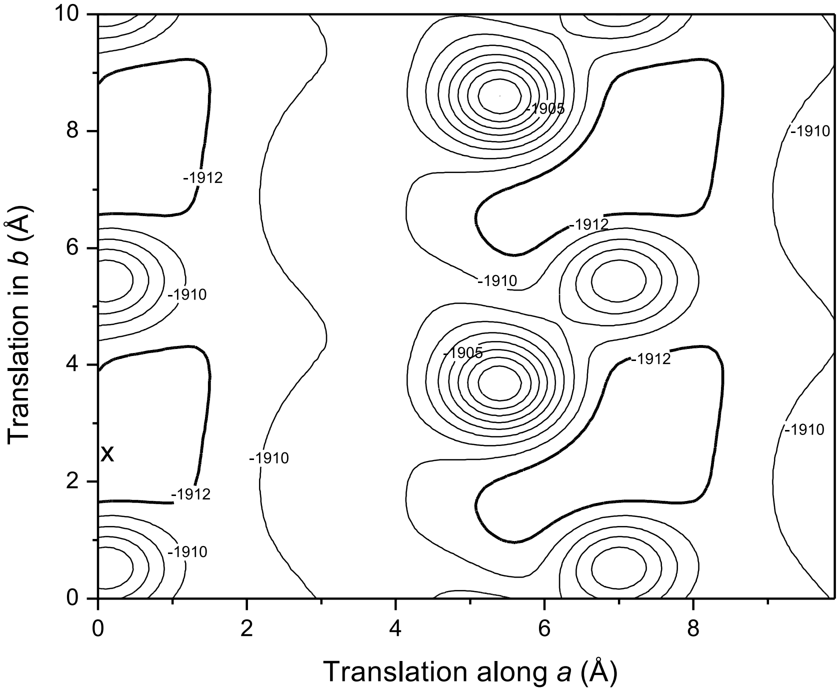

Fig. 2. Contour plot of the total potential energy as a function of translation of one crystal along the *a*, *b* directions. The global minimum is with a translation of 0.2 Å in the *a* direction and 2.5 Å in the *b* direction (labeled x). The region inside the thickest lines represent the possible arrangements with minimum energy of the opposing folds. The origin corresponds to the mirrored folds placed 'knuckle-to-knuckle'.

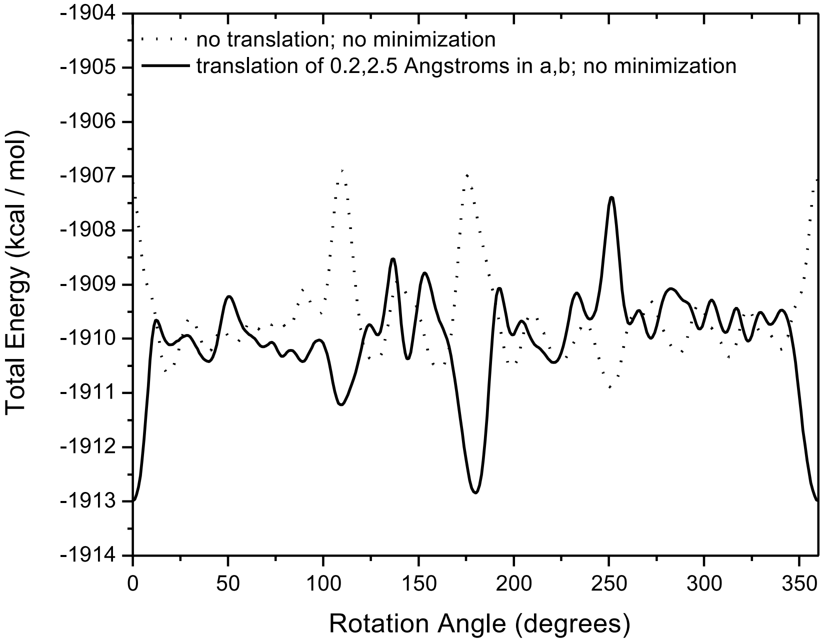

Fig. 3. The total potential energy of the system with respect to the rotation angle (about the principle *c*-axis) of one fold surface in contact with the other fold surface. Peaks represent unfavorable packing angles at this separation distance. The dotted line represents the initial system of opposing mirror image folds that were rotated with respect to each other. The solid line is the same system, initially translated to a position of minimum potential energy from Fig. 2 (0.2 Å in the *a* direction and 2.5 Å in the *b* direction) prior to rotation.

minimization by rotation of one of the two arrays with respect to the other.

By allowing the sample to relax at small rotations (0.5° increments) near the minima, the total energy is further reduced at a slight clockwise rotation of 3°, although this is only ∼1 kcal/mol lower than the translation minimum structure at the original rotation setting. The 3° corresponds approximately with experimental observations of the rotations of subsequent layers and might influence the rotation resulting from screw dislocations [37–39].

As discussed previously [35], the surface energy with respect to the melt state can be determined by the equation:

$$\sigma_e = [E - n(\Delta H_f - T\Delta S_f)]/A$$

*E* is the excess energy of the surface with respect to the crystal, $\Delta H_f$ is the crystal heat of fusion, $\Delta S_f$ is the crystal entropy of melting, *A* is the basal area of the unit cell, and $n=2$, corresponding to the two surfaces. The parameters of heat of fusion ($\Delta H_f = 4.11$ kJ(mol $CH_2)^{-1}$) and entropy of melting (($\Delta S_f = 9.91$ J(mol $CH_2)^{-1})K^{-1}$) are available from experimental and computational results [41–44]. Experimental values of the excess energy of the surface ($\sigma_e$) range from 0.071–0.095 J/m$^2$ [43–46].

To arrive at a computational value of the excess energy of the surface with respect to the crystal and melt, the total potential energy of the atoms involved in the fold is calculated in comparison to the same number of atoms within the inner region of an experimentally derived bulk crystal model [41]. The experimental bulk crystal model was allowed to relax to the COMPASS forcefield by carrying out an ultra-fine minimization (by the method defined previously), the unit cell dimensions changed slightly to $a=6.953$ Å and $b=4.754$ Å. Using the average basal area of the crystal (from the fold surface and the bulk crystal model) an energy of the crystal surface with respect to the bulk crystal and the PE melt of 0.185 J/m$^2$ was obtained. The calculated excess energy of the surface is almost twice the experimental value of 0.075–0.095 J/m$^2$, although much lower than the values yielded by previous simulation studies [35].

Possible reasons for the discrepancy between these simulations and experimental results include parameterization of the commercial force field used and the fact that experimentally there is some amount of roughness between the epitaxial layers.

## 4. Conclusions

The computed epitaxial arrangements with minor translation and rotation between crystals and others not given here [35] could influence the rotational packing of successive layers in multi-layer crystals resulting from screw dislocations [37–39]. They also reduce the computed excess surface energy with respect to the melt. However, they do not completely eliminate the discrepancy between the present results of modeling and the analysis of experimental data. Nevertheless, the current force field and method of analysis yield lower values of the excess energy with respect to the melt than did earlier modeling methods, possibly due to different methods of parameterization for the two forcefields [35]. With combined translation, rotation and minimization, lower energy juxtapositions of the crystals resulting from energetically favorable epitaxial arrangements were found.

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