The simplest model of polymer crystal exhibiting polymorphism.

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Almost all the polymer crystals have several polymorphic modifications. Their structure and existence conditions, as well as transitions between them are not understood even in the case of the 'model' polymer polyethylene (PE). For analysis of polymorphism in polymer crystals, we consider the simplest possible model of polymer chain: an extended flat zigzag made of 'united' atoms (replacing CH₂-groups in PE chain); the united atoms belonging to different zigzags interact via Lennard-Jones potential. Analysis of potential of interaction between such zigzags allowed to predict the structure of five possible equilibrium lattices in polymer crystal built out of such zigzags. Molecular dynamics simulation of the crystal built out of flexible zigzags showed that, depending on model parameters (dimensions of the zigzag and equilibrium distance of Lennard-Jones potential), one to three of these lattices are stable in bulk at low temperatures. We have determined the model parameters at which the existing stable lattices are analogous to the ones observed in real PE and linear alkanes. The triclinic lattice has the lowest potential energy, then follows the monoclinic lattice, and the orthorhombic lattice has the highest energy, exactly as in full atomic (with hydrogens) molecular dynamics models.

INTRODUCTION

Polymorphism is an attribute of polymer crystals. It is pronounced even in the simplest, 'model' polymer polyethylene (PE) [-CH₂]ₙ. The stable low-temperature phase in its linear odd n-alkanes is the orthorhombic (O) one, in its even n-alkanes - the triclinic (T) one up to n=24 and the monoclinic (M) one when 26 < n < 34 [1]. PE melt and solution crystallization gives O folded-chain crystallites, while on substrates [2, 3] and after polymerization inside nanochannels [4] there is a large amount of non-O (M and T) crystallites. At higher temperatures, one can also see a series of rotator phases in n-alkanes [5], and the hexagonal conformationally disordered phase in PE [6].

There exists the long history of study of PE phases depending on pressure and temperature. Starting with the works by Seto [7], the transitions between orthorhombic and monoclinic phases were widely investigated (see, for example, [8–10] and references in them; for a review, see [11]). On the other hand, the P-T phase diagram near the triple point melt-orthorhombic-hexagonal phases of PE was very early obtained [12] and then many times specified depending on length of PE chains, samples morphology and thermal history. But, in spite of all the efforts, the exact place of M and T phases on this diagram has never been established; the character of their instability is still unclear. Almost at any pressure, they normally coexist with the O phase. The pressure, at which they appear and the rate at which they transform back to the O phase, depend on mode of preparation of the samples (compare, for example, [7] and [13]). The understanding of the structure of these lattices can shed light on this unsolved problem.

One usually treats polymorphic modifications in molecular crystals in the framework of the 'closest packing' approach [14], considering number of 'contacts' between atoms in different lattices. This approach, as well as molecular mechanics studies [15], does not allow to say which interactions between molecules in a lattice are principal and what balance of forces forms every lattice. Correspondingly, one can not say which influence on the lattice is able to destroy its system of couplings and to provide the transition to another lattice. For example, in PE, T and M phases appear under pressure [7, 13], tension [16] and shear deformation[17]. But the needed directions of influence and resulting modes of deformation are still not understood.

To analyze a coupling between two molecules in a molecular crystal, one is to have their potential of interaction in treatable (better analytical) form. In the case of PE, it is natural to suppose that the details of the potential determined by hydrogen atoms are not principal for the system of couplings in the lattice. Then one can replace CH₂-groups by 'united' atoms (UA), and the chains in the lattice - by flat extended zigzags made of the UA.

However, it is a common opinion probably since 1980th [18] that 'the UA approximation does not provide a good representation of the crystal structures of alkanes' [19]. Indeed, we saw [20, 21] that, at some model parameters, the only crystal phase at low temperatures is a M lattice, different from the M lattice of PE. The other model parameters can even give a mobile hexagonal phase at 300K [19]. Therefore, all the works on crystalline phases in PE and alkanes use the full atomic (FA) model (with hydrogens) in spite of 'an order of magnitude increase in the processor time compared to the UA case' [19].

The goal of this article is to analyze equilibrium crystal lattices present in UA PE model at different model...
parameters, compare them with the lattices present in a realistic FA model of PE (taking into account hydrogen atoms) and to find the parameters at which the stable in bulk at low temperatures lattices are analogous to the ones observed in the FA model - and in real PE and linear alkanes.

The FA model that we will use as a standard was introduced in [22]. It uses generally accepted Amber99 force field [23] and gives the results on energies and densities of PE lattices similar to the ones obtained in other realistic empirical force fields [15, 24].

GEOMETRIC PARAMETERS OF UA PE MODEL.

UA PE model is widely used in modelling of properties of liquid and gaseous n-alkanes. The review [25] compares different sets of constants for simulation of fluid properties. We shall dwell on geometric parameters responsible for the presence of polymorphism in crystalline phase.

Van-der-Waals interaction of two UA belonging to different zigzags and placed \( r \) apart is normally described by 6-12 Lennard-Jones potential:

\[
U_{LJ} = \varepsilon \left( \frac{R_0^{12}}{r^{12}} - \frac{2R_0^6}{r^6} \right) \tag{1}
\]

The first evident geometric parameter of the model is the degree of ‘collectivity’ of interactions between UA, the ratio \( r_0 = R_0/c \), where \( c \) is longitudinal period of the PE chain. The more is \( r_0 \), the more UA of the neighboring zigzags take part in generation of the potential near an atom [26]. For example, in the Amber99 force field [23], for hydrogen-hydrogen, hydrogen-carbon and carbon-carbon interactions, the values \( r_0 \) equal to 1.166, 1.331 and 1.497 correspondingly. This parameter is widely varied in different simulations.

The second geometric parameter is the same in all but one of the works. Namely, UA are as a rule placed on carbon atoms, although, intuitively, it seems more adequate to shift united force centers closer to the hydrogens in the carbon atoms. According to work [25], this model gives the best agreement with experimental data in modelling of fluid properties of n-alkanes. We did not divide force and mass centers of UA, and placed a united atom on the bisector of the angle between hydrogen atoms, keeping the longitudinal period \( c \) of the PE chain and changing the distance \( d \) between the two rows of UA (fig. 1). In such an approach, we explicitly introduce the natural geometric characteristic of a flat zigzag, the ratio \( d_0 = d/c \), as the second geometric parameter of the model. When a united atom shifts from carbon to the point between hydrogens, \( d_0 \) changes from 0.337 to 0.843.

FIG. 1: Choice of the UA’ positions relative to the PE chain. Carbon (large) and hydrogen (small) atoms are white, UA are black, the bonds between the UA are dashed.

EXTREMA OF POTENTIAL OF INTERACTION BETWEEN TWO EXTENDED PARALLEL ZIGZAGS OF UA.

If we accept that two UA interact according to (1), then, if \( r_0 \) is reasonably large, \( r_0 > 1.115 \), the potential of interaction of one united atom with an infinite row of UA can be obtained by Poisson summation formula (see fig. 2(1)) where the first two terms quite suffice [26]:

\[
W_1 (k_0, \beta, \zeta) = \frac{3}{16} k_0 \varepsilon \left( J_0 (k_0, \beta) + J_1 (k_0, \beta) \cos (\zeta) + J_2 (k_0, \beta) \cos (2\zeta) + ... + J_m (k_0, \beta) \cos (m\zeta) + ... \right) \tag{2}
\]

where \( k_0 = 2\pi r_0 \), \( \beta = 2\pi b/c \), \( \zeta = 2\pi z/c \),

\[
J_0 (k_0, \beta) = \left( \frac{k_0}{\beta} \right)^{11} \frac{21}{32} - 2 \left( \frac{k_0}{\beta} \right)^5.
\]

The function \( J_0 (k_0, \beta) \) has a minimum equal to \(-1.43132\) at the point \( \beta = \beta_0 = B_0 k_0 \), \( B_0 = 0.9471316 \), and the function \( J_1 (k_0, \beta) \) can be very good approximated by an exponent near the point \( \beta_0 \):

\[
J_1 (k_0, \beta) \approx A_1 (k_0) \exp \left( -\Lambda(k_0) (\beta - \beta_0) \right),
\]

\[
A_1 (k_0) = \frac{2}{3} k_0^5 \exp \left( -\beta_0 \right) f_1 (\beta_0, k_0),
\]

\[
\Lambda(k_0) = 1 - \left. \frac{\partial f_1 (\beta, k_0)}{\partial \beta} \right|_{\beta = \beta_0} f_1 (\beta_0, k_0),
\]
I \[\theta\] gination as C in fig. 2. Finding potential \(W_1\) of an infinite row of UA at the point \(P\) as a function of \(b\) and \(z\). (2) Finding potential of interaction \(W_4\) between two zigzags. We show the projection of the zigzags on a plane orthogonal to their axes. The arrow points from the row of even atoms to the row of odd atoms of one zigzag. Black circle denotes the row in which zeroth atom belongs to the projection plane, white circle - the row in which the nearest to the projection plane atoms are at the distance \(c/2\) from it. We find \(W_4\) as a function of the distance \(D\) between the zigzags, their setting angles \(\theta_1\) and \(\theta_2\), and the shift \(z\) of the second zigzag along its axis from the projection plane. When \(z = 0\), the rows of even and odd atoms of the second zigzag also become 'black' and 'white' correspondingly. (3) Extrema of \(W_4\). In the sketches, we show only the arrows introduced on step (2); here, we imply that the rows of atoms are 'black' and 'white'. The lowest in energy coupling (the absolute minimum) has notation A, the higher extrema - notation B, C,... and so on.

\[
f_1(\beta, k_0) = k_0^6 \sqrt{\frac{1}{120\pi}} \left( \frac{945 + 945\beta + 420\beta^2 + 105\beta^3 + 15\beta^4 + \beta^5}{\beta^5} \right) - 2 \left( \beta^2 + 3\beta + 3 \right) / \beta^5
\]

To obtain the energy of interaction \(W_4\) between two zigzags (per 1 united atom), one is (see fig. 2(2)) to sum four terms of the type \(W_1\) (2), namely, the energy of two successive UA of one zigzag in the presence of two rows of another zigzag (and to divide by four). Unfortunately, only in the case of proximity of the zigzags to round cylinders \(d/D \sim d_0/r_0 = 1\) the function \(W_4\) can be adequately presented by the first terms of its Fourier series in angles \(\theta_1\) and \(\theta_2\). This condition does not hold in models exhibiting polymorphism in crystal lattices. Therefore, we found the extrema numerically as a sum of the mentioned four terms.

It is evident that \(\zeta = 0\) or \(\pi\) for equilibrium configurations. Taking \(\zeta = 0\) for definiteness sake, we obtained four (physically different) stationary points (see fig. 2(3)): A \((\theta_1 = \pi/2, \theta_2 = -\pi/2)\), B \((\theta_1 = \pi/2, \theta_2 = \pi/2)\), D \((\theta_1 = 0, \theta_2 = 0)\), E \((\theta_1 = 0, \theta_2 = \pi)\) similar to the ones in dipole-dipole interaction between electrical or magnetic dipoles. There are four more couplings designated as C in fig. 2(3). We did not draw arrows here, because all four combinations are possible, although the setting angles are a little different.

**TABLE I:** Distances \(y_S = D_S/R_0\) and energies \(w_S = W_4/E\) of equilibrium configurations of two zigzags (extrema of \(W_4\) listed in fig. 2(3)). The presented numerical values are calculated for model parameters \(G_4\) \((d_0 = 0.647, r_0 = 1.541)\). In other cases, the extrema and their order are the same, the numerical values slightly differ.

| extremum | \(y_S\) | \(w_S\) |
|----------|--------|--------|
| E        | 1.351  | -1.604 |
| D        | 1.323  | -1.745 |
| C        | 1.117  | -2.599 |
| B        | 0.931  | -3.681 |
| A        | 0.912  | -3.894 |

Among the listed couplings, A is a stable minimum, the rest stationary points are saddles. B is unstable in \(z\) direction (slides into A), C - in \(\theta_2\) direction (slides into B or A), D - in any direction in \((\theta_1, \theta_2)\) plane, as well as E, which is also unstable in \(z\) direction. The equilibrium distances \(y_S = D_S/R_0\) and energies \(w_S = W_4/E\) \((E(r_0, \varepsilon) = 1.6862\varepsilon)\) in these configurations are listed in Table I. The unit of energy \(E(r_0, \varepsilon)\) is chosen so that the first term in (2) has minimum equal to (-1).

**FORMATION OF EQUILIBRIUM LATTICES.**

We accept that structure of lattices is basically determined by interactions of a zigzag with 6 (or may be 8) zigzags of its first coordination sphere. Let us sketch a lattice as a set of arrows (introduced in fig. 2) representing zigzags in the projection plane orthogonal to the axes of the zigzags (see fig. 3).

Lattices based on A and B couplings: T and M1.

Geometrically, it is impossible to build a lattice using only the strongest and stable A couplings. One can form a row of arrows (for example, horizontal) so that every two neighboring arrows point in opposite directions (one - up, the second - down), and this will be a stable structure; but one still is to build a two-dimensional pattern from these rows. Combining the rows, one can not avoid forming couplings of D and E types between molecules in neighboring rows. As a result, we get a T lattice.

In it, A couplings in horizontal rows store about twice energy than the couplings between the rows (compare the energies of A, D and E couplings in Table I) and prevent the zigzags from rotation. E couplings are unstable regarding the shift of the zigzags along their axes, and this instability is compensated by the others couplings.

T lattice built out of rows with A couplings and having couplings of D and E types between rows may happen to be energetically less favorable than lattice M1 built out...
FIG. 3: Sketches of possible types of equilibrium lattices built out of zigzags interacting through potential having extrema presented in fig. 2 (3). Every lattice consists of (horizontal) rows of zigzags connected by equilibrium couplings: T - A, M₁ - B, O - C, M₂ - D. In real phases (see fig. 4), not only the couplings between rows but also the couplings forming rows may be slightly out of equilibria.

of rows with B couplings but having only D couplings between the rows.

A separate row with B couplings is an equilibrium structure, but it is unstable regarding the shift of any zigzag along its axis. In lattice M₁, the rows with B couplings stabilize by cohesion with each other: the arising couplings of D type are stable in z direction and compensate the instability of B couplings.

In both lattices T and M₁, the couplings D and E between rows are off their equilibria (although the forces are small), and every zigzag needs two couplings with the neighboring row to keep its setting angle.

Lattices using C and D couplings: O and M₂.

In lattice M₂, horizontal D couplings in rows do not form this lattice but rather are its vulnerability. The strongest couplings are the non-equilibrium ones between rows, intermediate between B and D, and designated as BD in fig. 4. They appear in both lattices M₂ and O. Again, to maintain the equilibrium, every zigzag needs two different BD couplings with another row. In lattice M₂, the setting angles of zigzags in D couplings may be off their equilibria, and BD couplings 0-1 and 1-2 may have different lengths, and so one of these couplings may be closer to B than another.

There can be at least two different equilibrium O lattices. In both of them, the couplings 0-2 and 1-2 (fig. 4, at the bottom) are equivalent and therefore the sum of the setting angles of zigzags θ₁ and θ₂ is π. In lattice O₁, θ₂ − θ₁ < π/2, in lattice O₂, θ₂ − θ₁ > π/2.

As we remember, the coupling C is unstable regarding rotation of zigzag 2 (see fig.2) and stable regarding rotation of zigzag 1. In accord with it, in O lattice, the zigzag is prevented from rotation basically by its neighbors for which arrows are aligned along the direction to the zigzag. Two other C couplings give almost flat potential, and BD couplings only shift a little the minimum of the energy.

CHOICE OF MODEL PARAMETERS FOR PE.

To find the point the best corresponding to PE in the rectangular area of reasonable parameters, we selected 140 points in the rectangle (intersections of grid lines in fig. 5) and studied possible equilibrium lattices in every point.

In the computational cell, we put 4 rigid zigzags parallel to z axis (more exactly, two UA from every of 4
To the experiment in directions of its edges in (X, Y). The computational cell was repeated nine times in the space of 16 variables starting at structures M. For the full Lennard-Jones energy of the zigzags, we imposed periodic boundary conditions. In all three directions, we imposed periodic angles of the zigzags differ from π/2 and −π/2, contrary to the experiment [7], and so possible candidates for PE can not lie in the domain ‘distorted T’.

Lattice O₂, corresponding to O lattice of real PE, exists everywhere except for 60% grey domain designated as ‘no O₂’. The setting angle θ₁ changes from ~30° in the upper part of the rectangle to 45° at the boundary with ‘no O₂’ domain. Lattice O₁ is present everywhere, and has lower energy than lattice O₂.

Lattice M₂, corresponding to M lattice of real PE, exists everywhere except for the 40% grey domain designated as ‘M₁’ where the only minimum of M type is lattice M₁. In the hatched domain ‘M₂+M₁’ these lattices coexist, and lattice M₂ has lower energy.

So, in the rectangle, only the points not painted in grey can be possible candidates for modelling of PE. Among them, the points belonging to the line G₄-G₆ have the density equal to the density of PE at low temperatures. So, it looks reasonable to select the point for PE in the domain bounded by a dashed polygon.

To make more precise choice, we compared the sizes of the lattices in several points on the line G₄-G₆ and in the FA MD model. The results are presented in Table II. One can see that the proportions of the lattices in toto approach the ones in FA model when we move from the point G₆ to the point G₇. Besides, the dynamical behavior of the crystal will probably be closer to the real one in the points with less dₒ because mass centers of UA will be closer to carbons as it is in real PE.

The chosen dashed polygon in fig. 5 is divided into two principally different zones. On the left, the models have four different lattices: T (ground state), M₂, O₁ and O₂; and O₁ was never found in real PE or alkalines. On the right, there is even five lattices: T (ground state again), M₂, O₁, M₃ and O₂, where two ‘superfluous’ lattices O₁ and M₁ are again lower in energy than the widespread at high temperatures lattice O₂. The natural question is: are the found lattices really present?

![FIG. 5: Domains of existence of different lattices depending on model parameters (for details, see section ). The points the best corresponding to real PE lie in the white area of the domain bounded by dashed polygon; the point G₆ is our best choice.](image)

| Lattice | G₆ | G₅ | G₄ | G₇ | FA PE |
|---------|----|----|----|----|-------|
| T       | 3.30 | 3.40 | 3.52 | 3.56 | 3.9   |
| Dₒ₁ (A) | 5.38 | 5.19 | 5.07 | 4.91 | 5.25  |
| Dₒ₂ (D) | 5.13 | 5.10 | 4.99 | 4.83 | 4.37  |
| θ₁      | 97  | 90  | 90  | 90  | 84    |
|        | 3.48 | 3.56 | 3.64 | 3.64 | 4.15  |
| Dₒ₁ (B) | 4.84 | 4.81 | 4.79 | 4.70 | 4.74  |
| Dₒ₂ (D) | 5.32 | 5.19 | 5.06 | 4.84 | 4.36  |
| θ₁      | 70  | 73  | 78  | 81  | 70    |
|        | 4.80 | 4.75 | 4.68 | 4.55 | 4.82  |
| Dₒ₁ (BD) | 4.18 | 4.22 | 4.25 | 4.22 | 4.25  |
| θ₁      | 33  | 34  | 36  | 36  | 47    |

**TABLE II: Lengths Dᵢⱼ of the couplings (in angstroms) and setting angles of the zigzags (in degrees) in lattices T, M₂ and O₂ (fig. 4) at different model parameters (in points shown in fig. 5) in comparison with FA model. In the brackets, we point out the type of the coupling.**
as phases in the model or are they somehow unstable? Indeed, our minimization problem was solved only in 16-dimensional space, and we definitely could block some modes of transformation between lattices, and some of the lattices may prove to be saddles, and not minima.

**STABILITY OF EQUILIBRIUM LATTICES IN UA PE MODEL - MD SIMULATION.**

The quickest way to answer the question put in the previous section is to carry out a MD simulation of all these lattices in large enough sample, in the framework of UA PE model having corresponding geometrical parameters, but with normal flexible zigzags, having all mobile UA. We took as a computational cell a parallelepiped having 120 zigzags 80 UA long packed into expected lattices. Because we are interested in stability in bulk, we imposed periodic boundary conditions in all three directions (and so the zigzags became 'infinite'). But, because we are interested in the easiest conversions between lattices, we opened a way for transformations closed in real experiments. Namely, we allowed the computational cell to change its shape (3 lengths and 3 angles) through uniform change of distances between atoms - according to the arising stresses (local stresses averaged over the sample). So, we facilitated conversions between lattices close in sizes - if the sample is able to preserve momentum and angular momentum during the conversion. In real experiments, martensitic transitions in bulk normally go through splitting samples into domains because this way of transformation is closed.

The exact values of force constants one uses in the model (the value \(\varepsilon\) in Lennard-Jones potential (1), rigidities of bonds between UA, of valence and torsional angles in zigzags) are not really important when one studies behavior of lattices at low temperatures. We carried out the MD experiments at T=1K, and used force constants close to the ones chosen by Toxvaerd [27]. Our force constants are listed in [21], except for the value \(\varepsilon\), which sometimes was taken to be equal to 0.16 kcal/mol instead of 0.12 kcal/mol. To maintain the temperature, a collisional thermostat [28, 29] was used with the parameters \(m_0 = 1\) a.m.u. and \(\lambda = 5.5\) ps\(^{-1}\), and a Berendsen barostat [30] was used for maintaining pressure in 1 atmosphere.

We carried out MD simulations of all obtained in the previous section lattices at model parameters corresponding to typical points (having different sets of equilibrium lattices) in fig. 5: \(G_1, G_2, G_3, G_T\) and \(G_4\).

One gets the point \(G_1\) \((d_0 = 0.337, r_0 = 1.673)\) if one puts UA on carbon atoms and then chooses \(R_0\) so that, at temperature \(T=300\)K, the density of the resultant crystal \((M_1)\) coincides with the density of O lattice of PE. In \(G_1\), we expected two lattices, \(M_1\) (ground state) and \(O_1\) (which is present everywhere). Lattice \(M_1\) appeared to be stable, \(O_1\) transformed into ground state \(M_1\). The mode of transformation is very simple and evident; the setting angle \(\theta_1\) (see fig. 4) grows up to \(90^\circ\) and the setting angle \(\theta_2\) drops down to \(90^\circ\), the sample slightly changes its sizes and we get an accurate \(M_1\) lattice. This transformation can so easily take place because the rotation of a couple of zigzags exactly conserves angular momentum. So, in the point \(G_1\), there is only one stable phase, as was already known [20].

In the point \(G_2\) \((d_0 = 0.337, r_0 = 1.273)\), with UA placed on carbons but having more 'local' interactions between atoms than in the point \(G_1\), we expected the lattices \(M_2\) and again \(O_1\). Both of them proved to be stable, and so, in the point \(G_2\), we have two stable phases.

In the point \(G_3\) \((d_0 = 0.493, r_0 = 1.528)\), we expected \(M_1\), \(T\), \(O_1\) and \(O_2\). \(O_1\) transforms (exactly as in the point \(G_1\)) into the ground state \(M_1\), the rest lattices are stable. So, in point the \(G_3\), we have 3 stable phases.

In the point \(G_T\) \((d_0 = 0.584, r_0 = 1.549)\), corresponding to the choice made by Toxvaerd [27] for liquid alkanes, we expected all the possible lattices in the order \(T, M_2, O_1, M_1\) and \(O_2\). Only two lattices, the lowest \((T)\) and the highest \((O_2)\) in energy proved to be stable phases, the rest lattices transformed into the ground state \(T\). We can conclude that the domain 'M2+M1' should be excluded from the area of possible candidates for PE.

In the point \(G_4\) \((d_0 = 0.647, r_0 = 1.541)\), we expected \(T, M_2, O_1\) and \(O_2\). Only lattice \(O_1\) transformed into \(T\); the rest lattices are stable.

So, in the point \(G_4\), we have three low-temperature phases exactly analogous to the phases observed in real PE (fig. 4). The ground state of the system is \(T\) phase, followed by \(M_2\) and then \(O_2\), exactly as in the FA PE model. The densities of the phases differ from the ones in the FA PE model less than by 1%.

**CONCLUSION.**

Potential of interaction of two flat parallel rigid (infinite) zigzags built out of UA has 5 different extrema. Connecting zigzags by couplings close to these extrema, one can build 5 different equilibrium crystal lattices, including lattices \(T, M_2\) and \(O_2\) observed in PE and alkanes at low temperatures. So, the presence of hydrogens is not necessary for the presence of polymorphism in this polymer crystal: UA PE model catches the main features of interaction between zigzags and provides all the needed polymorphic modifications in the crystal built out of such zigzags. However, these equilibrium lattices can be saddles as well as local minima in potential energy of the crystal lattice depending on geometrical parameters of the model. In different domains of parameter space, one to five of these lattices can be local minima.

Unfortunately, the usual choice of UA positions on carbons eliminates \(T\) lattice as a minimum and, at (also usually used) very long-range interactions between UA, also
eliminates O lattice. This is the reason why UA model has been in disrepute. But the shift of UA to hydrogens leads to appearance of minima for both lattices T and O₂.

However, a lattice can be a minimum in the space of variables of possible crystal lattices having corresponding symmetry restrictions, but to be a saddle in full space of variables, because the symmetry restrictions may block the modes of transformation between lattices. The simplest way to check if an equilibrium lattice is a phase (meaning stable in bulk at low temperatures) is to carry out a MD simulation of it in a large enough sample, with all mobile UA. We did it for several typical points in space of model parameters and found that UA model can have one to three phases. These three phases may be (the point G₄) or not be (the point G₃) analogous to phases in PE. This narrowed the area for possible candidates for modelling of PE to the white part of the domain bounded by dashed polygon in fig. 5. Based on analysis carried out up to now, we would say that the best choice for PE is point G₄, although, after the further investigation of temperature behavior and phase transitions, the other points in the area can prove to be more suitable.

In the framework of UA model, one can observe phase transitions in polymer crystals in reasonable time of calculations, which makes this model (having properly chosen parameters) a useful instrument for studying features of polymorphic modifications and martensitic transitions in polymer crystals.

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