

# On the influence of thermal motion on the crystal structures and polymorphism of even *n*-alkanes

Jacco van de Streek,<sup>a†</sup> Paul Verwer,<sup>a,b</sup> Piet Bennema<sup>a</sup> and Elias Vlieg<sup>a\*</sup>

<sup>a</sup>Department of Solid State Chemistry, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands, and <sup>b</sup> Centre for Molecular and Biomolecular Informatics, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

† Present address: Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Correspondence e-mail: vlieg@sci.kun.nl

Received 27 November 2001  
Accepted 4 March 2002

Discrepancies between the crystal structures of short *n*-alkanes as obtained from experiment and as obtained from molecular mechanics tended to worsen at longer chain lengths. The same holds for the relative stabilities of the two experimentally observed polymorphs. In this paper it is argued that the discrepancies are caused by thermal effects, and that the triclinic polymorph is the most stable polymorph for all chain lengths at 0 K. A phase transition is predicted but has yet to be found experimentally. Current force fields cannot reproduce the experimental observations without explicit introduction of temperature by means of molecular dynamics.

## 1. Introduction

Long-chain compounds, found in membranes, liquid crystals, petrol, polyethylene and triacylglycerols (or fats, the main ingredient of margarine and chocolate), do not easily form crystals suitable for single-crystal X-ray analysis. The crystals are thin platelets or needles that are easily bent, and usually exhibit micro twinning. Long-chain compounds also tend to form many polymorphs, each of them possessing specific physical properties, and some technique to solve their structures is required. Powder diffraction is a good alternative, but a powder diffraction pattern contains much less information. Molecular modelling can hopefully provide enough additional data to solve these structures from powder data. It is not until after the crystal structures have been elucidated that calculations at the atomic level, regarding *e.g.* the relative stabilities of the various polymorphs, are possible.

The major part of long-chain compounds is made up of *n*-alkyl chains and understanding the interactions between *n*-alkane molecules is the basis for understanding the more complicated systems. In turn, it seems plausible to regard *n*-octane as a computational-friendly model system for the interactions in *n*-alkanes in general. Hence, starting from the complex systems, much of the problem can be reduced to a thorough understanding of the crystal structure of *n*-octane.

*n*-Octane (or sometimes *n*-hexane, the crystal structure of which is homomorphously isomorphous) has been used in the parameterizations or validations of most, if not all, force fields for organic molecules. During these computations, however, complications arose. While parameterising the MM3 force field, Lii & Allinger (1989) noted systematic errors in the cell parameters of *n*-octane-type crystals upon energy minimization and speculated that these errors are caused by the anisotropy of the interactions. Dillen (1990) developed a force field for which the absolute errors in the cell angles were between 0.0 and 0.7°, except for the angle  $\gamma$  of *n*-octane, for which the absolute error was 2.8°. Williams (1994) noted that

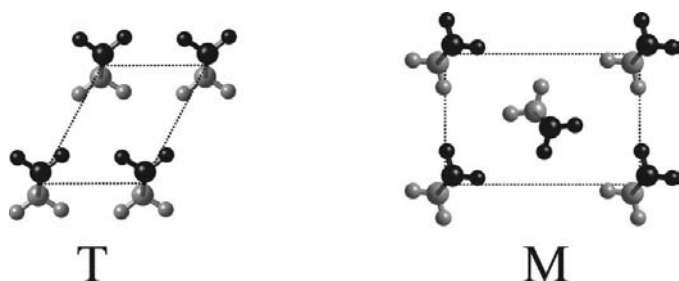
the error in the orientation of the *n*-octane molecule was even worse, and suspected that this was caused by an inadequate description of the electrostatics. He improved this description by adding 12 off-atom sites, but the effect on the crystal structure was not as large as expected.

*n*-Octane itself being just a model system, we set out to explore the consequences of these errors for more relevant systems. Do they simply disappear, turning out to be an artefact of the chain being too short, or do they become worse? The most common alkyl chain lengths in biologically and industrially relevant systems are  $\cdot\text{C}_{16}\text{H}_{33}$  and  $\cdot\text{C}_{18}\text{H}_{37}$ , so it seemed natural to check the performance of force fields validated on the *n*-octane crystal structure when applied to *n*-alkanes longer than 16 carbon atoms. We are not aware of any earlier attempts to do so. *n*-Alkanes crystallize in a different crystal structure when the chains are longer than 24 carbon atoms. To establish convincingly that current force fields are suitable for longer *n*-alkanes, this transition must also follow from the calculations. Hence, calculations were performed on *n*- $\text{C}_{20}\text{H}_{42}$  because it is between *n*- $\text{C}_{16}\text{H}_{34}$  and *n*- $\text{C}_{24}\text{H}_{50}$ , and on *n*- $\text{C}_{36}\text{H}_{74}$  because it is well above *n*- $\text{C}_{24}\text{H}_{50}$ .

Two problems became apparent from force-field calculations on *n*- $\text{C}_{20}\text{H}_{42}$  and *n*- $\text{C}_{36}\text{H}_{74}$ . First, the geometrical discrepancies between the experimental and the energy-minimized crystal structures of *n*-octane are even worse for *n*- $\text{C}_{20}\text{H}_{42}$ . Second, the thermodynamic stability of the *n*- $\text{C}_{20}\text{H}_{42}$ -type crystal structure with respect to the *n*- $\text{C}_{36}\text{H}_{74}$ -type crystal structure observed experimentally is not reproduced computationally. We will address these problems by comparing three approaches: the properties as calculated with current force fields, molecular dynamics simulation with current force fields and the properties as calculated with a special-purpose force field.

## 2. Experimental crystal structures and phase behaviour of *n*-alkanes

Turner (1971) has reviewed the experimental crystal structures and phase behaviour of *n*-alkanes. Pure (>98%) *n*-alkanes with an even number of carbon atoms crystallize in either of two space groups. Crystals of *n*- $\text{C}_6\text{H}_{14}$  through to *n*- $\text{C}_{22}\text{H}_{46}$  are triclinic, space group  $P\bar{1}$ , whereas *n*- $\text{C}_{30}\text{H}_{62}$  and upwards



**Figure 1**  
Chain packings of the T polymorph and the M polymorph. Top view, along the chains. The bigger spheres represent carbon atoms, the smaller spheres hydrogen atoms. Grey atoms are at  $z = \frac{1}{4}$ , black atoms at  $z = \frac{3}{4}$ .

crystallize in the monoclinic space group  $P2_1/c$ . Both series are homologically isomorphous and will be denoted by T for triclinic and M for monoclinic. *n*- $\text{C}_{24}\text{H}_{50}$  through to *n*- $\text{C}_{28}\text{H}_{58}$  constitute a transition region and have been observed in both polymorphs. Interestingly, when both polymorphs are observed for the same compound, the T polymorph crystallizes at lower temperature, while the M polymorph crystallizes at higher temperature (Madsen & Boistelle, 1976). The crystal structures of several members of the triclinic series have been solved, namely *n*- $\text{C}_6\text{H}_{14}$ , *n*- $\text{C}_8\text{H}_{18}$  (Norman & Mathisen, 1961*a,b*; Mathisen *et al.*, 1967; Boese *et al.*, 1999), *n*- $\text{C}_{18}\text{H}_{38}$  (Nyburg & Lüth, 1972), *n*- $\text{C}_{20}\text{H}_{42}$  (Nyburg & Gerson, 1992) and *n*- $\text{C}_{24}\text{H}_{50}$  (Nyburg & Gerson, 1992). Only one member of the monoclinic series has been solved, namely *n*- $\text{C}_{36}\text{H}_{74}$  (Shearer & Vand, 1956).

The main difference between the T and the M polymorph is the lateral arrangement of the molecules within a layer. The carbon atoms of an all-*trans* *n*-alkane molecule lie in a plane; in the T polymorph, all planes are parallel, while in the M polymorph, neighbouring planes are perpendicular (Fig. 1). Polyethylene, the ultimate long-chain compound without end-groups, is usually observed as the ‘M’ polymorph (Kavesh & Schultz, 1970), although the ‘T’ polymorph has been observed as well.

The application of high pressure favours the T polymorph, even at chain lengths above *n*- $\text{C}_{30}\text{H}_{62}$  (Turner, 1971). This indicates that the T polymorph is the densest. The absolute values of the densities can be calculated directly from the crystal structure. The equivalence of the densities thus obtained to those obtained through more sophisticated methods has been established by Vand (1953) and Cole & Holmes (1960).<sup>1</sup>

## 3. Molecular modelling

Before molecular mechanics can be applied to a problem, it should first be proved whether the calculations can reproduce the available experimental data. For *n*-alkanes, these are the data described in the previous section.

The most straightforward way of applying force fields is energy minimization. Temperature (thermal motion) does not play a role in these static calculations, and hence they represent the situation at 0 K. In force fields parameterized against experimental crystal data, the average effect of temperature on the structure is implicitly present, as crystal structures are usually determined at room temperature.

### 3.1. Current force fields

The obvious explanation for the T → M transition observed as a function of chain length is that at short chain lengths the end-groups dominate, while at longer chain lengths the influence of the chain takes over. In other words, the end-groups favour the T polymorph, whereas the chains favour the M

<sup>1</sup>Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0106). Services for accessing these data are described at the back of the journal.

**Table 1**  
Comparison of force fields.

	Charges	Intramolecular terms
DREIDING/X6	No†	Yes
Compass	Yes	Yes
CVFF	Yes	Yes
Mooij <i>et al.</i> (1999)	No†	Yes
Gavezzotti & Filippini (1995)	No	No
Williams (1994)	Yes	No

† Inclusion of charges made no difference.

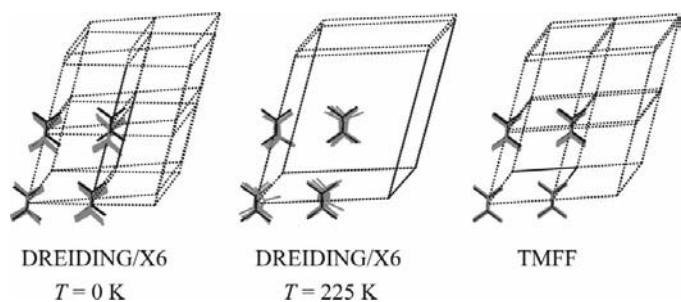
polymorph. Thermal vibration is negligible according to Mnyukh (1963). If this were the case – and as will be shown later, it is not – the stability of the T *versus* M polymorph should be controlled by enthalpy only and calculations on static crystal structures optimized with a force field should reproduce the experimental observations.

Models for both the T and the M polymorph were built for all even *n*-alkanes from *n*-C<sub>6</sub>H<sub>14</sub> through to *n*-C<sub>36</sub>H<sub>74</sub> starting from the crystal structures of *n*-C<sub>20</sub>H<sub>42</sub> and *n*-C<sub>36</sub>H<sub>74</sub> and using the fact that the series of structures are homologously isomorphous (Nyburg & Potworowski, 1973).

Several force fields, namely DREIDING/X6 (Mayo *et al.*, 1990), compass (MSI, 1998), CVFF (Hagler *et al.*, 1979), and the force fields of Mooij *et al.* (1999), of Gavezzotti & Filippini (1995) and of Williams (1994), were used. Some of these come with charges, and some of these come with intramolecular force-field parameters; this is summarized in Table 1. The effect of the intramolecular terms on the energy-minimized crystal structures was negligible, as was the effect of charges (van de Streek *et al.*, 2002).

Only the results obtained with DREIDING/X6 will be given here: the results obtained with the other force fields were similar. The van der Waals interactions for the DREIDING/X6 force field are given by

$$E_{\text{vdw}}(R) = D_0 \{ [6/(y-6)] \exp[y(1-R/R_0)] - [y/(y-6)](R/R_0)^{-6} \}, \quad (1)$$



**Figure 2**  
Superimpositions of the experimental crystal structures (black) of the T polymorphs of *n*-C<sub>*m*</sub>H<sub>2*m*+2</sub> and the same structures minimized (grey) using DREIDING/X6 (*m* = 20), after molecular dynamics calculations with DREIDING/X6 at 225 K (*m* = 12, only four of the 75 molecules are shown), and minimized using TMFF (*m* = 20). Top view, along the chains.

where *R* is the distance between the two atoms, *D*<sub>0</sub> is the van der Waals well depth, *y* is a scaling parameter and *R*<sub>0</sub> is the equilibrium distance.

We would like to stress here that our experience has shown that the weak van der Waals interactions and the resulting flat energy landscape require a comparatively sophisticated energy minimization procedure, especially for the longer chains. The ‘Smart Minimizer’ as implemented in the *Cerius*<sup>2</sup> program (MSI, 1998) was used; this minimizer uses a sequence of algorithms starting with the robust steepest descent algorithm and ending with a truncated Newton algorithm, implying that second derivatives are used in the final steps of the minimization. The steepest descent algorithm alone was found to be unsatisfactory for long-chain-compound crystal structures. Ewald summation was used for both the van der Waals interactions and, when included, the Coulomb interactions, with the accuracy set to  $1 \times 10^{-4}$  kcal mol<sup>-1</sup> (1 cal  $\simeq$  4.19 J). When the alkane chains exceeded a length of 16 carbon atoms, the convergence had to be set to RMS (root mean square) force =  $1.0 \times 10^{-3}$  kcal mol<sup>-1</sup> Å, maximum force =  $5.0 \times 10^{-3}$  kcal mol<sup>-1</sup> Å,  $\Delta E = 1.0 \times 10^{-4}$  kcal mol<sup>-1</sup>, RMS displacement =  $1.0 \times 10^{-5}$  Å, maximum displacement =  $5.0 \times 10^{-5}$  Å, RMS stress =  $1.0 \times 10^{-3}$  GPa, maximum stress =  $5.0 \times 10^{-3}$  GPa (the ‘High Convergence’ option in *Cerius*<sup>2</sup>). Since the positions of hydrogen atoms are usually ill-determined in X-ray data, they were always placed in calculated positions before a full optimization of the crystal structure was carried out.

Overlapping models of the experimental and the energy-minimized crystal structures of *n*-C<sub>20</sub>H<sub>42</sub> are shown in Fig. 2 (left). It can be seen that current force fields do not seem to be capable of reproducing the experimental crystal structure for a class of compounds as simple as the *n*-alkanes.

The dashed lines in Figs. 3(a) and 3(b) show the energies and densities of the minimized crystal structures. Similar results were obtained with the other force fields. The energies presented here are the crystal energies of the energy-minimized crystal structures, including the intramolecular contributions. Subtracting the energy of a molecule in the gas phase (to obtain sublimation enthalpies) would not have changed the relative order of the energies or the point where the lines cross. Not only do the lines fail to cross at or near *n*-C<sub>26</sub>H<sub>54</sub>, which could be explained by assuming a small error in the interactions of the end groups such that the intercepts are slightly off, but moreover the slopes of the energy curves are such that the T polymorph is calculated to become increasingly more stable as the chain length increases, whereas the opposite is observed experimentally. Furthermore, current force fields do not seem capable of reproducing the relative energies of the two crystal structures.

### 3.2. Molecular dynamics

The effect of thermal motion is usually a more or less isotropic increase in the cell parameters *a*, *b* and *c*. This is not supposed to influence the structure greatly, and thermal expansion is incorporated implicitly in force fields para-

meterized against crystal data. The situation might be different for *n*-alkanes, which exhibit a very anisotropic expansion.

An NPT molecular-dynamics simulation was carried out using *Cerius*<sup>2</sup> (MSI, 1998) to assess the influence of thermal motion explicitly. The homologically isomorphous crystal structure of *n*-C<sub>12</sub>H<sub>26</sub> was interpolated from the experimentally known crystal structures of the triclinic polymorph as described by Nyburg & Potworowski (1973) and energy minimized. A supercell consisting of  $5 \times 5 \times 3 = 75$  independent *n*-C<sub>12</sub>H<sub>26</sub> molecules was built with overall dimensions  $a = 20.82$ ,  $b = 22.05$ ,  $c = 51.22$  Å,  $\alpha = 83.69$ ,  $\beta = 67.36$ ,  $\gamma = 78.48^\circ$ . The system was equilibrated with a time step of 0.001 ps at  $T = 225$  K ( $T_m \approx 265$  K) and  $P = 0.0001$  GPa. 80 ps were simulated with a time step of 0.0001 ps after equilibration. The DREIDING/X6 force field was used, but for this molecular-dynamics simulation the equilibrium C–H bond length was shortened from 1.09 Å to 1.00 Å (the effect of this change in the bond length on the minimized crystal structure was negligible). The interaction cut-off was set to 10 Å. The calculations took four weeks on three R10000 processors. The average cell parameters during equilibrium were  $\langle a \rangle = 21.3 \pm 0.1$ ,  $\langle b \rangle = 22.9 \pm 0.1$ ,  $\langle c \rangle = 52.1 \pm 0.2$  Å,  $\langle \alpha \rangle = 83.2 \pm 0.4$ ,  $\langle \beta \rangle =$

$66.3 \pm 0.5$ ,  $\langle \gamma \rangle = 74.2 \pm 0.8^\circ$ . Fig. 2 (middle) shows a part of the configuration obtained 5.4 ps after equilibration, superimposed on the interpolated experimental structure.

Comparing the results with DREIDING/X6 at 0 K and at 225 K (Fig. 2), it can be seen that although the 0 K calculations do not reproduce the crystal structure very well, explicitly including temperature solves this problem.

### 3.3. A new force field

Molecular-dynamics simulations are computationally expensive. A simple van der Waals-only force field would be desirable for a problem as simple as the crystal structure of an *n*-alkane. Hence, rather than attempting to include temperature explicitly or to add new interaction terms, we tried to derive phenomenologically a van der Waals-only force field which could reproduce the crystal structure of *n*-C<sub>20</sub>H<sub>42</sub> at room temperature. In particular, the effective size of the atoms should increase because of the thermal motion.

The starting van der Waals parameters were taken from a preliminary set of Mooij *et al.* (1999) data. Dispersion damping and all electrostatics including polarization were discarded, leaving equation (1). Off-diagonal van der Waals parameters were calculated using the arithmetic combination rule. One van der Waals parameter at a time was slightly changed, after which the experimental structure was minimized with the resulting force field. If the newly minimized structure resembled the experimental structure more closely than the previously minimized structure, the change was kept, and discarded otherwise. This procedure was repeated iteratively for the three parameters for both carbon and hydrogen until no further improvement could be gained.

Fig. 2 (right) shows the experimental crystal structure of *n*-C<sub>20</sub>H<sub>42</sub> and the structure minimized with the new force field. The new force field implicitly incorporates the thermal motion of the *n*-alkanes, and hence will be named the 'Thermal Motion Force Field', or TMFF. The resulting parameters are given in Table 2.

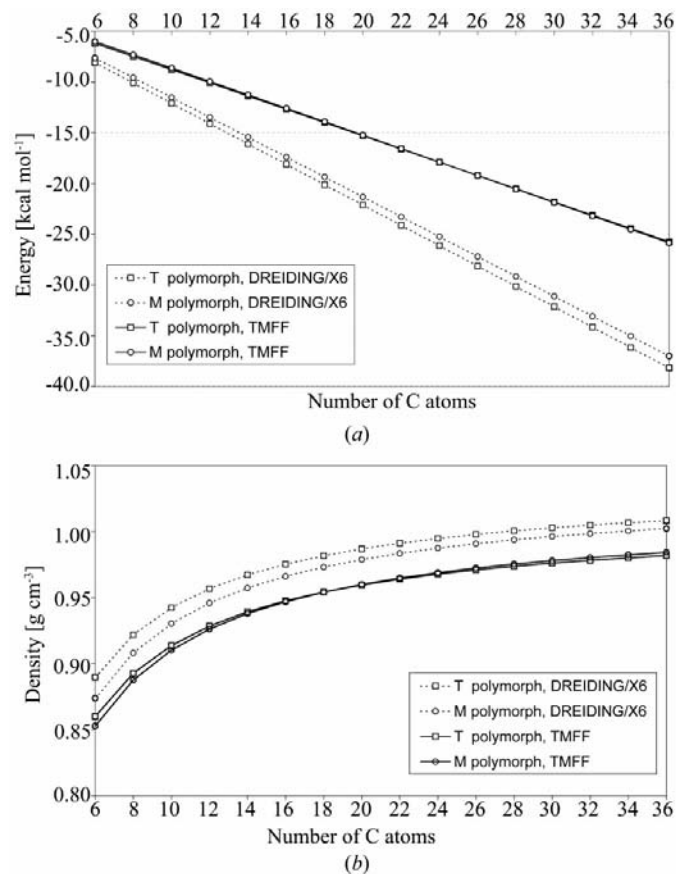
The TMFF parameters were optimized exclusively against an example of the T polymorph. The influence of TMFF on the M polymorph was established by energy minimization of the crystal structure of the 'M' polymorph of polyethylene. The reproduction of the crystal structure of the M polymorph is also improved by using TMFF (Fig. 4).

The last check remaining is the relative stabilities of the two polymorphs. The solid lines in Fig. 3 show the energies and densities of the crystal structures minimized with TMFF. The transition between the T and the M polymorph is reproduced correctly.

Thus, both crystal structures and the energetics are very well reproduced, using just a simple van der Waals force field.

## 4. Discussion

The force-field calculations with DREIDING/X6 at 0 K give the correct order of the densities; T is always denser. Moreover, these computational 0 K results agree with the low-



**Figure 3**

(a) Lattice energies of the T and the M polymorphs for *n*-C<sub>6</sub>H<sub>14</sub> through to *n*-C<sub>36</sub>H<sub>74</sub> minimized using DREIDING/X6 and TMFF. (b) Densities of the T and the M polymorphs for *n*-C<sub>6</sub>H<sub>14</sub> through to *n*-C<sub>36</sub>H<sub>74</sub> minimized using DREIDING/X6 and TMFF.

**Table 2**

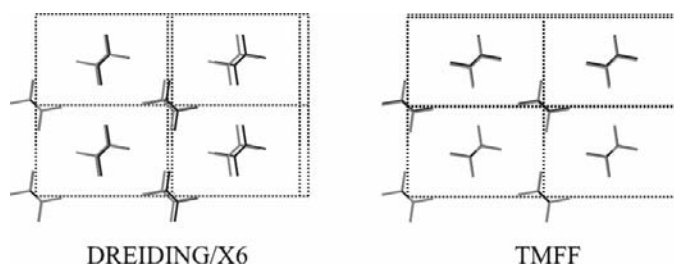
van der Waals parameters in equation (1) for the DREIDING/X6, the Mooij *et al.* and the TMFF force field.

	$D_0$ (kcal mol <sup>-1</sup> )	$\gamma$	$R_0$ (Å)
C, DREIDING/X6	0.0951	14.034	3.8983
C, Mooij <i>et al.</i> (1999)	0.07844	14.887	4.1353
C, TMFF	0.075	14.5	4.30
H, DREIDING/X6	0.0152	12.382	3.195
H, Mooij <i>et al.</i> (1999)	0.01297	11.769	2.9985
H, TMFF	0.010	12.0	3.10

temperature experimental results for  $n$ -C<sub>28</sub>H<sub>58</sub> as far as the relative stabilities of the T and the M polymorphs are concerned. Apparently the force field performs well for environments with decreased molecular motion (either low temperature or high pressure). According to Kitaigorodskii (1965), the densest polymorph should have the lowest energy. This rule too is satisfied by the calculations with DREIDING/X6 at 0 K. However, the agreement between the minimized crystal structure and the experimental crystal structure, which was solved at room temperature, remains unsatisfactory.

Introducing temperature into the DREIDING/X6 force field by means of molecular dynamics causes substantial changes in the simulated crystal structure of  $n$ -C<sub>12</sub>H<sub>26</sub> towards the experimental structure. These changes mainly concern the angle  $\gamma$  and the orientation of the molecule. The disadvantage of using molecular dynamics is the great demand in computer time. TMFF has the same improved agreement with experiment, but the calculations require just minutes per crystal structure.

The most striking change in the van der Waals parameters between those of Mooij *et al.* (1999) and TMFF (Table 2) is the increase in the radii of the carbon and the hydrogen atoms. This increase can be related to the experimentally accessible atomic displacement parameters (ADPs), and indeed the ADPs of especially the methyl groups of  $n$ -C<sub>20</sub>H<sub>42</sub> are larger than those found in other organic molecular compounds. The ADPs measure the spatial extents of the atoms in the crystal structure and are a measure for *e.g.* their degree of thermal motion. This links the new force field to the molecular-dynamics simulation, and comparing the middle and right diagrams in Fig. 2 shows the clear similarity between the two approaches. It is apparently possible to mimic this dynamic

**Figure 4**

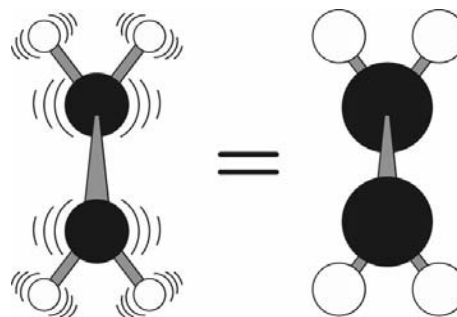
Superimpositions of the experimental crystal structure (black) of the 'M' polymorph of polyethylene and the same crystal structure minimized (grey) using DREIDING/X6 or TMFF. Top view, along the chains.

thermal motion by a static increase of the size of the atoms, as indicated schematically in Fig. 5. More general force fields, which have been parameterized against the crystal structures of several families of compounds and not only those of the  $n$ -alkanes, do not cater for the rather extreme thermal motion observed in  $n$ -alkanes.

Although the expansion of the carbon atoms in TMFF seems isotropic, since it was the isotropic van der Waals radius that was increased, the resulting expansion upon energy minimization is in fact very anisotropic. From a molecular mechanics point of view, the two directions perpendicular to the chain are nonbonded interactions and therefore affected by the increase, whereas the direction along the chain is dictated by bonded interactions only and is unaffected by the change in the van der Waals radius. This agrees with the physical reality, as is clear from the anisotropic ADPs of the methyl groups of *e.g.*  $n$ -C<sub>20</sub>H<sub>42</sub>, which are 13.2, 12.8 and 7.4 × 100 Å<sup>2</sup> along **a**, **b** and **c**, respectively (Nyburg & Gerson, 1992).

The radius of the hydrogen atom is slightly smaller in TMFF than it was in DREIDING/X6. In DREIDING/X6, the hydrogen radius was parameterized on the crystal structure of  $n$ -hexane using fixed values for carbon; if the radius of the carbon atom was slightly too small to reproduce the  $n$ -hexane structure accurately, the hydrogen radius might have been assigned a value that is slightly too large to compensate partially for the smaller carbon radius.

Although the new force field was optimized exclusively against the crystal structure of  $n$ -C<sub>20</sub>H<sub>42</sub>, other shortcomings in DREIDING/X6 have disappeared as well. Not only did the energy-minimized crystal structures of both the T and the M polymorphs improve, but also, more importantly, the relative stabilities of the T and the M polymorphs are now correct. The transition point is calculated to be near  $n$ -C<sub>25</sub>H<sub>52</sub>, while at room temperature  $n$ -C<sub>24</sub>H<sub>50</sub> crystallizes as the T polymorph and  $n$ -C<sub>28</sub>H<sub>58</sub> crystallizes as the M polymorph. The exact agreement might be fortuitous, but it does show that apparently TMFF energies correspond to calculations at room temperature. An estimate of the van der Waals parameters for other temperatures can be obtained by linear interpolation or extrapolation.

**Figure 5**

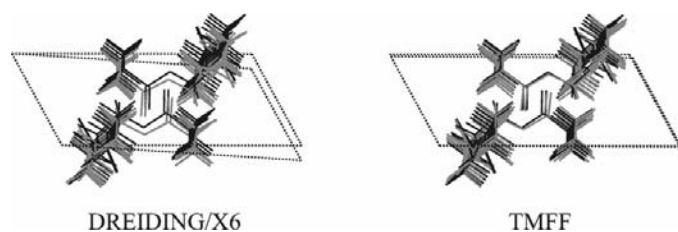
Equivalence of small moving atoms and large static atoms. Carbon atoms are shown in black, hydrogen atoms are shown in white. Top view, along the chain.

Note how the densities of these ‘room-temperature’ crystal structures changed accordingly, albeit slightly out of step with the energies: the M polymorphs of  $n\text{-C}_{20}\text{H}_{42}$  through to  $n\text{-C}_{24}\text{H}_{50}$  are calculated to be denser than the T polymorphs for the same chain lengths, yet their energies are less favourable. The TMFF densities are lower than those of the structures minimized with DREIDING/X6, as expected. The crystal structures of the  $n$ -alkanes being so much closer to experiment, it goes without saying that the calculated density, as a derived property, has equally improved. For example, the experimental density of the M polymorph of  $n\text{-C}_{36}\text{H}_{74}$  at 293 K is  $0.9609(2)\text{ g cm}^{-3}$  (Vand, 1953), whereas DREIDING/X6 and TMFF give  $1.0023$  and  $0.9842\text{ g cm}^{-3}$ , respectively.

From our results we must conclude that at 0 K, the T polymorph is the stable polymorph for all chain lengths. Hence, the M polymorph of even  $n$ -alkanes of all chain lengths, including polyethylene, must have a phase transition to the T polymorph upon cooling. Conversely, the T polymorph of even  $n$ -alkanes of all chain lengths, including polyethylene, must have a phase transition to the M polymorph upon heating.

The  $T \rightarrow M$  transition has never been observed experimentally for a number of reasons. On heating the T polymorph, chain lengths under 24 carbon atoms melt before the transition occurs; for longer chain lengths a rotator phase appears, obscuring the transition. (It could be argued that the movement of the chains in the rotator phase, which is mainly in the **ab** plane, is nothing but the onset of the phase transition from T to M.) On cooling the M polymorph, the rotation of half of the molecules along their long axes by  $90^\circ$  will be a very difficult transition from a kinetical point of view. However, an as yet unexplained transition to a denser phase upon cooling has been found for the M polymorph of  $n\text{-C}_{36}\text{H}_{74}$  (Cole & Holmes, 1960). This might be the transition to the T polymorph, but the crystal structure of the new phase was not determined. We suggest that the best route for the observation of the transition is the very slow heating of the T polymorph of  $n\text{-C}_{28}\text{H}_{58}$ ; we are not aware of any attempts in this direction.

Apart from the obvious application to  $n$ -alkanes, calculations showed that TMFF is not generally transferable to other hydrocarbons, let alone other classes of compounds. This is not surprising, as TMFF incorporates the rather extreme thermal motion of  $n$ -alkanes, which is not found in other crystal

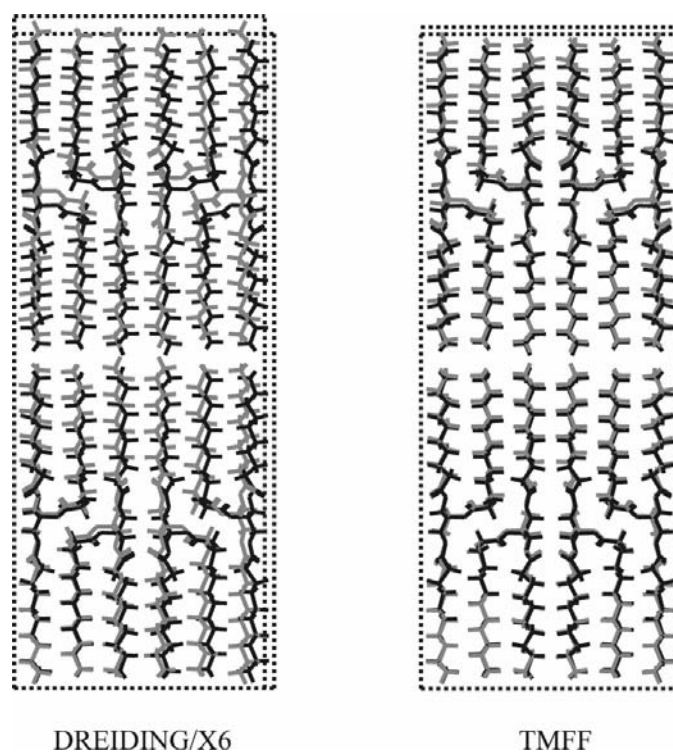


**Figure 6**  
Superimpositions of the experimental crystal structure (black) of the ‘T’ (=  $\beta$ ) polymorph of 10.10.10 and the same crystal structure minimized (grey) using DREIDING/X6 and TMFF. View along the  $c$  axis.

structures. There is, however, one important class of compounds for which TMFF outperforms DREIDING/X6: triacylglycerols. The experimental crystal structure of 1,2,3-tri- $n$ -dodecanoylglycerol (Gibon *et al.*, 1984), an example of the ‘T’ polymorph, behaves identically to the  $n$ -alkanes upon energy minimization with DREIDING/X6 and TMFF (Fig. 6). The energy-minimized crystal structure of 1,3-di- $n$ -decanoyl-2- $n$ -dodecanoylglycerol (Van Langevelde *et al.*, 2000), an example of the ‘M’ polymorph, is also substantially improved when using TMFF as compared with DREIDING/X6 (Fig. 7). The increased mobility of the atoms in the ‘M’ polymorph has been confirmed experimentally for triacylglycerols by  $^2\text{H}$  NMR studies (Eads *et al.*, 1992).

## 5. Conclusions

Computer simulations suggest that the transition from the T polymorph to the M polymorph on increasing chain length is not caused by the competition of the van der Waals energies of the end groups *versus* the chains, but by thermal motion. At 0 K, the T polymorph is the stable polymorph for all chain lengths. At higher temperatures, the relative stability of the two polymorphs of even  $n$ -alkanes is a function of both chain length and temperature. In general, a crystal structure will try to find a balance between packing as closely as possible so as to maximize the van der Waals energy, and packing as loosely as possible so as to maximize molecular motion.



**Figure 7**  
Superimpositions of the experimental crystal structure (black) of the ‘M’ (=  $\beta'$ ) polymorph of 10.12.10 and the same crystal structure minimized (grey) using DREIDING/X6 and TMFF. View along the  $b$  axis.

Our results indicate that electrostatics is not important to reproduce the crystal structures and energies of *n*-alkanes. van der Waals interactions are sufficient if thermal motion is taken into account explicitly through the use of molecular dynamics. For calculations on *n*-alkanes, the special-purpose force TMFF offers a fast alternative to molecular dynamics in cases where it is only the structure of the solid state that is important, e.g. during polymorph predictions, for which thousands of crystal structures have to be optimized. Molecular dynamics are recommended for calculating properties other than the static crystal structure.

H. A. J. Oonk and D. Mondieig are kindly acknowledged for their valuable discussions. The investigations were supported by the Netherlands Organization for Chemical Research (NWO-CW) within the framework of the PPM/CMS-Crystallization project. Unilever is kindly acknowledged for financial support.

## References

- Boese, R., Weiss, H.-C. & Bläser, D. (1999). *Angew. Chem. Int. Ed. Engl.* **38**, 988–992.
- Cole, E. A. & Holmes, D. R. (1960). *J. Polym. Sci.* **46**, 245–256.
- Dillen, J. L. M. (1990). *J. Comput. Chem.* **11**, 1125–1138.
- Eads, T. M., Blaurock, A. E., Bryant, R. G., Roy, D. J. & Croasmun, W. R. (1992). *J. Am. Oil Chem. Soc.* **69**, 1057–1068.
- Gavezzotti, A. & Filippini, G. (1995). *J. Am. Chem. Soc.* **117**, 12299–12305.
- Gibon, V., Blanpain, P., Norberg, B. & Durant, F. (1984). *Bull. Soc. Chim. Belg.* **93**, 27–34.
- Hagler, A. T., Dauber, P. & Lifson, S. (1979). *J. Am. Chem. Soc.* **101**, 5131–5141.
- Kavesh, S. & Schultz, J. M. (1970). *J. Polym. Sci. Poly. Phys. Ed.* **8**, 243–276.
- Kitaigorodskii, A. I. (1965). *Acta Cryst.* **18**, 585–590.
- Lii, J. H. & Allinger, N. L. (1989). *J. Am. Chem. Soc.* **111**, 8576–8582.
- Madsen, H. E. L. & Boistelle, R. (1976). *Acta Cryst.* **A32**, 828–831.
- Mathisen, H., Norman, N. & Pedersen, B. F. (1967). *Acta Chem. Scand.* **21**, 127–135.
- Mayo, S. L., Olafson, B. D. & Goddard, W. A. III (1990). *J. Phys. Chem.* **94**, 8897–8909.
- Mnyukh, Y. V. (1963). *J. Phys. Chem. Solids*, **24**, 631–640.
- Mooij, W. T. M., Van Duijneveldt, F. B., Van Duijneveldt-van de Rijdt, J. G. C. M. & Van Eijck, B. P. (1999). *J. Phys. Chem. A*, **103**, 9872–9882.
- MSI (1998). *Cerius<sup>2</sup>*. Version 3.9. Molecular Simulations Inc., San Diego, CA, USA.
- Norman, N. & Mathisen, H. (1961a). *Acta Chem. Scand.* **15**, 1747–1754.
- Norman, N. & Mathisen, H. (1961b). *Acta Chem. Scand.* **15**, 1755–1760.
- Nyburg, S. C. & Gerson, A. R. (1992). *Acta Cryst.* **B48**, 103–106.
- Nyburg, S. C. & Lüth, H. (1972). *Acta Cryst.* **B28**, 2992–2995.
- Nyburg, S. C. & Potworowski, J. A. (1973). *Acta Cryst.* **B29**, 347–352.
- Shearer, H. M. M. & Vand, V. (1956). *Acta Cryst.* **9**, 379–384.
- Streek, J. van de, Verwer, P., Bennema, P. & Vlieg, E. (2002). *J. Comp. Chem.* **23**, 365–370.
- Turner, W. R. (1971). *Ind. Eng. Chem. Prod. Res. Dev.* **10**, 238–260.
- Vand, V. (1953). *Acta Cryst.* **6**, 797–798.
- Van Langevelde, A., Van Malssen, K., Driessen, R., Goubitz, K., Hollander, F., Peschar, R., Zwart, P. & Schenk, H. (2000). *Acta Cryst.* **B56**, 1103–1111.
- Williams, D. E. (1994). *J. Comp. Chem.* **15**, 719–732.