

Polymer Communication

Simulation of chain folding in polyethylene: A comparison of united atom and explicit hydrogen atom models

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ABSTRACT

We performed a systematic study to show that the nicely folded lamellar structure of polyethylene chains derived from previous molecular simulations is a consequence of the use of the united atom model, which treats the CH₂ groups as a hard sphere. Simulations presented here with explicit hydrogen atoms show that the fold is not uniform, and that regularly aligned stems do not result. While it is known that polyethylene crystallizes with chain folded morphology, the irregular folding seen here is due to the neglect of the interactions between the hydrogen atoms attached to a carbon atom C_i and the atom C_{i+2} in the united atom model. We present this paper to point out how the choice of force fields is important for polymers with a high degree of crystallinity. We hope that this paper stimulates further work on developing united atom models that take into account terms that we show to dictate the polymer conformations, such as the interactions between atoms attached to carbon atom C_i and the atom C_{i+2} in polyethylene.

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1. Introduction

Molecular simulation of polymers and polymer analogues has advanced significantly in the last four decades. Refinement of force field parameters, novel simulation methodologies and the technological revolution in computing power indeed created a paradigm shift. An important aspect of polymer morphology is chain folding, and it was an area of intense activity and debate (as to whether it is adjacent or non-adjacent reentry of the chains) during the sixties and the seventies [1–10].

Using molecular dynamics (MD), Kavassalis and Sundararajan [11] performed atomistic simulations of chain folding in polyethylene. By varying the length of the chains, they rationalized the energetic reason for the experimental observation that chains of less than 150 CH₂ units in length do not fold. The major shortcoming of the results of Kavassalis and Sundararajan [11] was that the dimension of the chain folded lamella was only about 4 nm, whereas these were more than 20 nm as observed experimentally. These authors were able to account for larger lamellar dimensions in their subsequent publications [12,13] by reasoning that the torsional barrier has a significant role in chain folding and that a larger barrier than that in n-butane is required to account for the

dynamics of chains such as polyethylene, especially when a united atom approximation is used.

Since then, several publications [14–35] have appeared on the simulations of chain folding of polyethylene, using molecular dynamics, Brownian dynamics and Monte Carlo methods. Ignoring the higher torsional barrier used by Sundararajan and Kavassalis [12,13], most of these publications interpreted the short lamella obtained using the butane-like torsional barrier to be the nucleus for the further crystallization of PE, and chain growth on the initial nucleus has been simulated. A study of chain folding in the presence of fullerene has also been reported recently [35] by using the united atom model.

The basic approximation adopted by the authors of all such publications to date is the treatment of the CH₂ group as a hard sphere. This united atom approximation is the most elementary form of coarse grain modeling. Using this methodology, nicely folded lamella, with a combination of adjacent and non-adjacent reentry of chain segments were obtained in all published reports [14–35]. Such an united atom approach was favoured due to computational advantage, in terms of reduction in the number of atoms used for the simulation, as well as obviating the need for using smaller time steps for integration due to the presence of the hydrogen atom.

In this paper, we examine the effect of using explicit hydrogen atoms in the simulation of chain folding of PE. The explicit presence of hydrogen gives rise to non-bonded interactions which now

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become dependent on the torsional angle about the parent C–C bonds. For example, if we consider a chain of $(\text{CH}_2)_n$ from 1 to n , the interactions between hydrogens attached to C_i and C_{i+2} (see Scheme 1) are not effectively compensated by the united atom model, since the interaction between C_i and C_{i+2} is not included in the calculations. While the distance between C_i and C_{i+2} is invariant to torsional angle, the distances between H_i and C_{i+2} as well as the hydrogens attached to the latter depend on the torsional angle. Thus, the characteristics of chain folding can be expected to be different with the use of explicit hydrogens. We show that although the chain collapses during MD simulation, the inclusion of explicit hydrogens does not result in nicely folded lamellae thus far obtained by several authors, including Sundararajan and Kavassalis [11–13].

2. Simulation models and methods

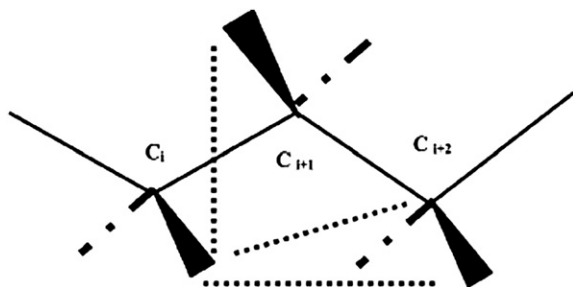
To test our hypothesis, five linear polyethylene chain models including three united atom models and two explicit hydrogen models with each containing 1000 backbone carbon atoms were used in this work. Table 1 summarizes the details of these models. Models 1 and 2 use the Dreiding force field 2.21 [36, see Table 2] with united atom approximation and explicit hydrogens, respectively. Model 3 uses the COMPASS force field [37, see Table 2], with explicit hydrogens. Models 4 and 5 examine the effect of using larger Lennard-Jones (LJ) σ values of 1.05σ and 1.10σ for the CH_2 group with united atom models, while all other intra- and intermolecular parameters used were default values in the original Dreiding force field 2.21.

The parameter σ enters the LJ function in the form of.

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

where σ is the distance at which the inter-atomic potential energy between a pair of atoms is zero, r is the distance between two atoms and ε is the depth of the potential well.

The Dreiding and COMPASS force fields were used as representative examples, since they differ in the form of the equations as well as in the parameter set. Dreiding [36] is a simple general force field, uses a 6–12 LJ function for van der Waals interactions and a simple equation for torsion energy with a 2 kcal/mol barrier for the C–C bond. The COMPASS force field was derived from a combined parameterization in which valence parameters were fitted to *ab initio* data and the van der Waals parameters were obtained by fitting MD-simulated and experimental cohesive energies and equilibrium densities. It uses a 9–6 expression for LJ function, and a torsion barrier of 0.275 kcal/mol. In terms of the torsion energy alone, both trans and gauche conformations are of equal energy in the Dreiding force field, but the latter is about 0.1 kcal/mol higher in energy in COMPASS which also uses cross coupling terms for unlike atom pairs.



Scheme 1. The dotted lines illustrate the interactions that are ignored in the united atom model.

Table 1

Force fields and hydrogen models used for the five polyethylene systems, each containing 1000 backbone carbon atoms.

Model	Force Field	Hydrogen Model
1	Dreiding with default intra- and intermolecular parameters	United Atom
2	Dreiding with default intra- and intermolecular parameters	Explicit
3	COMPASS with default intra- and intermolecular parameters	Explicit
4	Dreiding with $\sigma = 1.05$ times the default σ value of CH_2	United Atom
5	Dreiding with $\sigma = 1.10$ times the default σ value of CH_2	United Atom

Initial structures of all models were constructed in vacuum using the three states rotational isomeric state theory of Abe et al. [38] and subsequent energy minimization by using the conjugate gradient method. The resultant structures were then subjected to subsequent MD simulations in vacuum at 463 K (i.e., 190 °C, a temperature commonly used in the characterization of polyethylene liquids in practice) for as long as 1 ns or longer. The Nose canonical method along with velocity-Verlet algorithm [39] was employed for generating all of the MD trajectories. The integration time step was 1 fs. All simulations were carried out on a Silicon Graphics (SGI) workstation cluster along with the use of commercial software – Cerius² version 4.0 (Accelrys).

3. Results and discussion

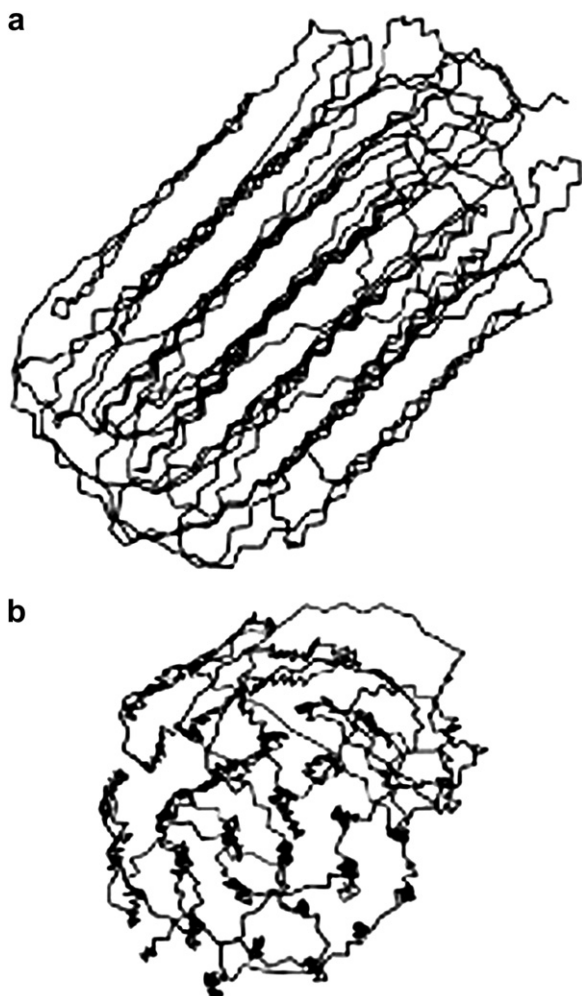
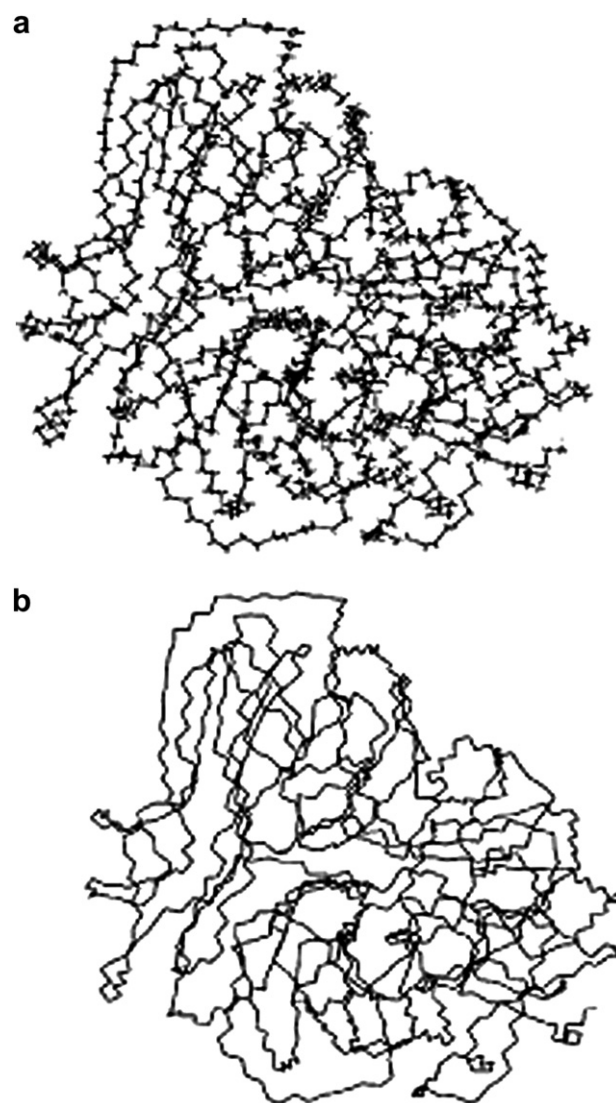
The results of the MD simulations after 1 ns at 463 K for each model listed in Table 1 are given in Figs. 1–4. It is clear from Fig. 1 for Model 1 with the united atom approximation, that the structure resembles the one obtained by Kavassalis and Sundararajan [11] as well as those reported by other researchers mentioned in the Introduction. The linear chain folded tightly with the chain segments aligning as a lamella. The stems are predominantly in the trans conformation, with the folds containing both trans and gauche conformers. However, Figs. 2 and 3 show that when explicit hydrogen models (Models 2 and 3) were used in the MD annealing, although the chain collapsed, the resultant structures did not form an ordered lamella. In particular, the collapsed structure of Model 2 (i.e., the explicit hydrogen model and use of the original Dreiding 2.21 force field) after 1 ns of MD annealing is essentially a globule (Fig. 2). It is worth noting that the same parameters were used in Models 1 and 2. However, when the COMPASS force field was used (Model 3), the resultant structure folded as an irregular lamella. It contains a slightly more ordered chain segments as compared to that of Model 2. However, the segments of the chain meander widely. As discussed above in the section on Simulation Models and Methods, compared to Dreiding, the torsional potential used in COMPASS has a greater difference in the torsional energy between the trans and gauche states and a lower torsional energy barrier. It was also noted that the 6–12 LJ function used in the Dreiding force field is hard in the repulsive region, whereas the 9–6 function is softer [37]. Nevertheless, chain segments in the collapsed structure of Model 3 do not form an ordered lamella as in Fig. 1. The difference between the structures of Models 2 and 3 can be attributed to the torsional expression and van der Waals parameters used in the respective force fields. The key finding here is that regardless of the potential used, united atom models yield chain folded structures significantly different from those of explicit hydrogen models.

As mentioned in Introduction, Sundararajan and Kavassalis [11] obtained nicely folded lamella using the united atom model and

Table 2

Functional forms used in DREIDING 2.21[36] and COMPASS force fields [37].

Interaction		DREIDING 2.21	COMPASS
Valence terms	Bond energy	$E_b = 1/2K_b(R - R_0)^2$	$E_b = \sum_b [k_2(b - b_0)^2 + k_3(b - b_0)^3 + k_4(b - b_0)^4]$
	Angle energy	$E_\theta = 1/2K_\theta(R - R_0)^2$	$E_\theta = \sum_\theta [k_2(\theta - \theta_0)^2 + k_3(\theta - \theta_0)^3 + k_4(\theta - \theta_0)^4]$
	Torsional energy	$E_\phi = \sum_{n=1}^2 1/2K_\phi n[1 \pm \cos(n\phi)]$	$E_\phi = \sum_\phi [k_1(1 - \cos \phi) + k_2(1 - \cos 2\phi) + k_3(1 - \cos 3\phi)]$
	Out-of-plane angle	$E_{inv} = K_{inv}(\cos \chi - \cos \chi_0)^2$	$E_\chi = \sum_\chi k_2 \chi^2$
	Cross-coupling terms		$E_{cross} = \sum_{b,b'} k(b - b_0)(b' - b'_0) + \sum_{b,\theta} k(b - b_0)(\theta - \theta_0)$ $+ \sum_{b,\phi} (b - b_0)[k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi]$ $+ \sum_{\theta,\phi} (\theta - \theta_0)[k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi]$ $+ \sum_{\theta,\theta'} k(\theta - \theta_0)(\theta' - \theta'_0)$ $+ \sum_{\theta,\theta',\phi} k(\theta - \theta_0)(\theta' - \theta'_0) \cos \phi$
Nonbond terms	Coulombic interaction	$E_{coul} = 332.0637 q_i q_j / \epsilon r_{ij} \text{erfc}(r_{ij}/\beta)$	$E_{coul} = \sum_{i,j} \frac{q_i q_j}{r_{ij}}$
	Van der Waals energy	$E_{vdw} = \epsilon_0 [(\sigma_0/R)^{12} - 2(\sigma_0/R)^6]$	$E_{vdw} = \sum_{i,j} \epsilon_{ij} [2(\frac{r_{ij}^0}{r_{ij}})^9 - 3(\frac{r_{ij}^0}{r_{ij}})^6]$

**Fig. 1.** Structure of Model 1 (Dreiding, United atom) after 1 ns of MD annealing at 463 K (a) side view, (b) end view.**Fig. 2.** Structure of Model 2 (Dreiding, explicit) after 1 ns of MD annealing at 463 K (a) all carbon and hydrogen atoms are shown, (b) only the backbone carbon atoms are shown for visual convenience.

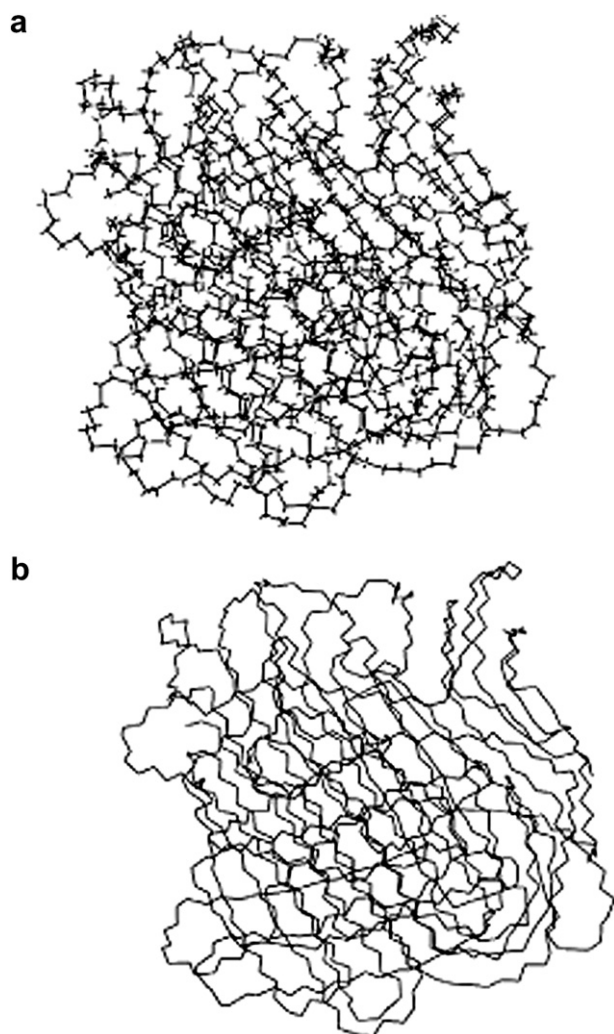


Fig. 3. Structure of Model 3 (COMPASS, explicit) after 1 ns of MD annealing at 463 K (a) all carbon and hydrogen atoms are shown, (b) only the backbone carbon atoms are shown for visual convenience.

Dreiding force field, although the lamellar dimension was small, similar to that shown in Fig. 1. In a subsequent publication, they increased the torsional barrier from 2 kcal/mol to 4–6 kcal/mol, using the same force field. The chain still folded nicely into a lamella, although the lamellar dimension increased to about 20 nm, in accord with experimental values.

The above results suggest that by including hydrogen atoms explicitly in a polyethylene model, it significantly alters the chain folding pattern. Despite the fact that hydrogen atoms are relatively small, the above results indicate that they inflict additional steric hindrances on the formation of hairpin structures making the polyethylene chain difficult to form a compact lamellar structure in these simulations. Therefore, it was speculated that the effect of using larger σ values for CH_2 in a united atom model might be similar to that of using explicit hydrogen atoms. Results shown in Fig. 4 confirm such speculation that after 1 ns of MD simulation, chains in Models 4 and 5 (with 5% and 10% larger σ values for CH_2 , respectively but with the use of the same torsional potential as for Model 1) did not show a sign of collapsing into a compact structure similar to that shown in Fig. 1.

Fig. 5 shows the torsional angle distribution of the structure at the end of the MD run, for the united atom, explicit hydrogen models and the united atom with 1.1 σ in the L-J function. It is seen



Fig. 4. Structures of united atom Models 4 and 5 (Dreiding) after 1 ns MD annealing at 463 K (a) Model 4 (1.05 σ), (b) Model 5 (1.1 σ).

that due to the lack of interactions involving the groups attached to C_i and C_{i+2} , the gauche angle distribution in the united atom model (Fig. 5a) is broad, ranging from about 70 to 120°. However, with explicit hydrogen (Fig. 5b), the distribution centers about $\pm 110^\circ$, and the non-staggered conformations are suppressed. The distribution of the trans conformation becomes more distinct and narrower than in the case of Fig. 5a. In the extreme, in the case of the united atom model with 1.1 σ (Fig. 5c), the distribution of the trans conformation becomes broad, the gauche states are suppressed, and the chain does not fold.

Note that the equilibrium populations of the carbon–carbon bonds in the trans and gauche states depend on the difference in the energy (non-bonded and torsional) of the two states while the extent of chain folding depends on the barrier between them. Such barrier consists not only of the torsional energy term but also the non-bonded interactions between atoms attached to a given bond. Thus, although the two force fields use different type of equations for the torsional and van der Waals terms, it is through the adjustment of the latter that they both reproduce the experimental ethane torsional barrier of 2.8 kcal/mol. Historically, the torsional energy term did not exist in conformational modeling using

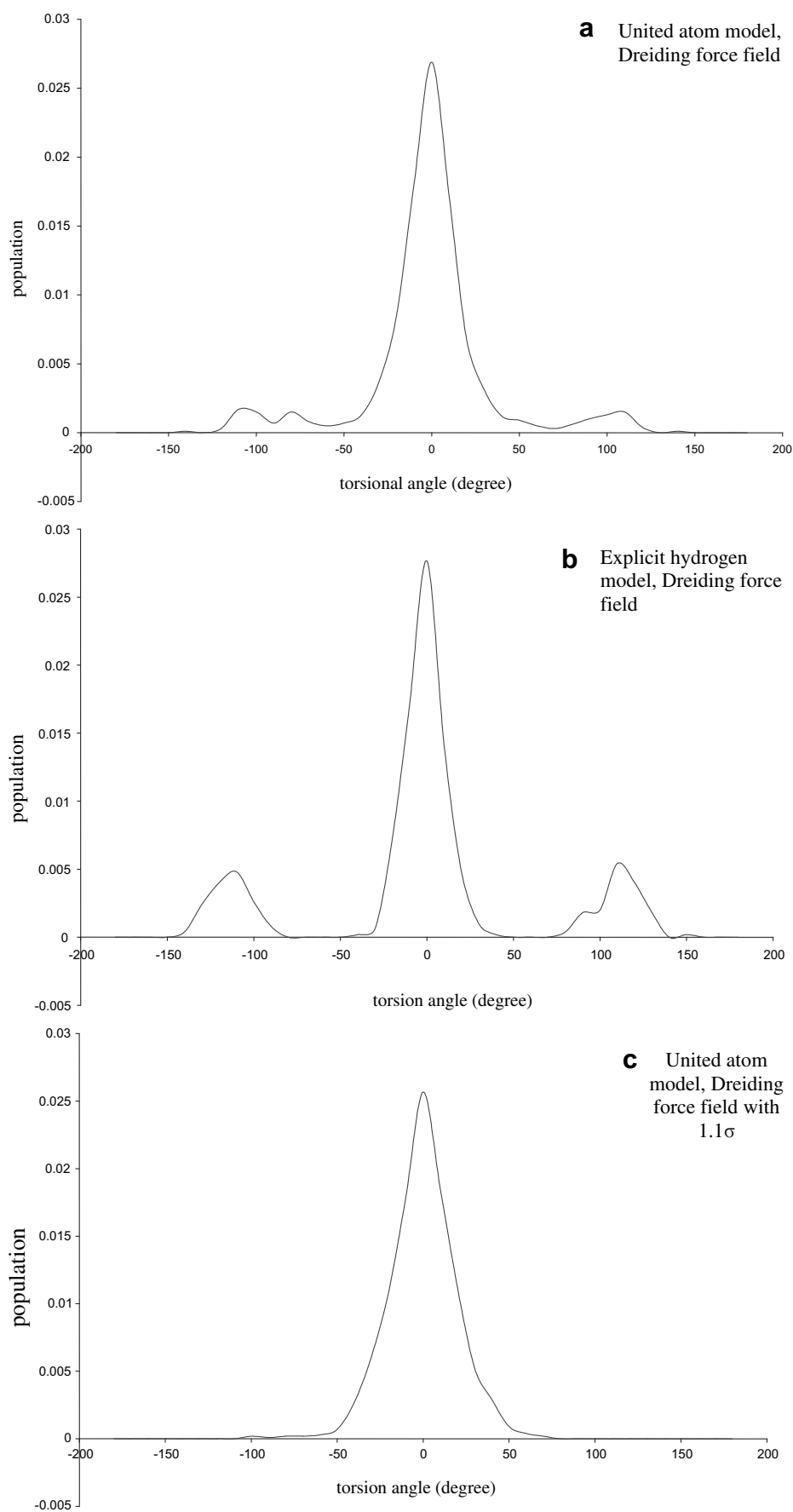


Fig. 5. Torsion angle distributions upon chain collapse, using Dreiding force field with (a) united atom model, (b) explicit Hydrogens and (c) united atom model with 1.1σ .

empirical methods prior to mid-1960s. Rao et al. [40] mention that since at that time the experimental energy barrier between the trans and eclipsed conformations could not be reproduced using the non-bonded energy term alone, a function for torsional energy was introduced. This was explained eloquently by Flory [41]. Thus, it is not only the energy barrier used in the torsional function, but also the non-bonded interactions that determine the kinetics of the transformation from a trans to a gauche conformation.

The key observation in the present work is that regardless of the force field used, explicit hydrogen models yield chain folded structures significantly different from those of united atom models. This is due to the non-inclusion of the interactions involving the hydrogen atoms attached to C_i and C_{i+2} carbons in the united atom model, as discussed above. This is demonstrated by comparing the results of Models 1, 2 and 3. Here, the Dreiding force field was used in both Models 1 and 2 (with the same energy parameters). And it is obvious that upon high temperature MD annealing at 463 K over the same period of time, Model 2 exhibited much less order and lack of lamellar formation, compared to Model 1. Such difference, especially the number of hairpins, is expected to persist even when longer MD annealing times are used. The collapse itself occurs within 100 ps of MD.

The result of Model 3, which uses a different torsional potential and LJ function also suggests that tightly chain folded lamellar structure could not be obtained when an explicit hydrogen model was used. However, the lower torsional barrier and soft van der Waals term in this model does lead to localized short lamellae. In the case of explicit hydrogen models, the cause is the steric effect as depicted in Scheme 1. The aim of this Communication is to simply point to this effect, and not the development of a force field in this paper to address it.

4. Conclusions

We show that although the united atom approximation is simple in terms of computational efforts, it does not represent the local interactions between hydrogen atoms on i and $i+2$ carbon atoms. It is in fact these interactions that govern the transition from trans to gauche conformation of a skeletal bond, which is necessary for chain folding. The nicely folded, short lamellae reported Kavassalis and Sundararajan [11], and several authors since, is a result of united atom potential. In this paper, we simply point to the consequence of not including these non-bonded near neighbor interactions in the united atom models used thus far. A judicious

mechanism to incorporate these terms in the united atom model is thus warranted.

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