

Master I Chemoinformatique - Deuxième Session (Juin 2009)

Examen de "Interactions inter- et intramoléculaires dans les systèmes complexes"
Enseignant : Rachel Schurhammer

Durée : 2h

Aucun document de cours n'est autorisé.

Calculatrice et Dictionnaire Français - Anglais autorisés.

1) Questions de cours :

- Donner et décrire en quelques lignes deux méthodes utilisées pour simuler des cristaux liquides.
- Quels types de problèmes peut engendrer un traitement strict par un cutoff des interactions à longues distance ? Quelles sont les alternatives que vous pouvez proposer pour pallier à ces problèmes ?
- Quels sont les différents moyens d'obtenir des paramètres de liaisons pour effectuer une simulation de dynamique moléculaire ?

2) Solvant implicite et explicite en dynamique moléculaire classique (DM) :

Dans les cas suivants, quel est, selon vous, le traitement le plus adéquat pour le solvant ? Justifier.

- Nitrobenzène liquide pur
- Complexation de l'ion K^+ par le 18C6 dans l'eau
- Ions Cl^- dans un cristal liquide

2) Simulations de polymères

Après lecture de l'extrait de la publication donnée en Annexe 1, répondez aux questions suivantes :

- Décrire le champ de force utilisé par les auteurs. En quoi est-il différent d'un champ de force "classique" comme AMBER ?
- Comment les chaînes de polymères sont-elles modélisées ?
- Décrire en quelques lignes le principe des simulations "coarse-grained".

- d) A quoi correspond la courbe donnée FIG 2 b) ? Quelles sont les implications sur la conformations de chaînes de polymères simulées ?
- e) Comment les interactions non-liées sont-elles traitées ?
- f) Quelle autre méthode de recherche conformationnelle les auteurs auraient-ils pu utiliser dans le cas de ce système ?

Annexe 1

Extrait de l'article :

"On the construction of coarse-grained models for linear flexible polymer chains : Distribution functions for groups of consecutive monomers"

J. Baschnagel, K. Binder, W. Paul, M. Laso, U.W. Suter, I. Batoulis, W. Jilge and T. Bürger
J. Chem. Phys. 1991, 95(8), 6014-6025

II. MONTE CARLO STUDY OF MODELS FOR POLYETHYLENE

Even for polyethylene, a chemically simple polymer chain, there is not yet complete agreement on the choice of a detailed model potential. The purpose of this section and the following one hence is twofold: (i) to test to what extent the distributions $P_n(l)$, $P_n(\vartheta)$ obtained from our coarse-graining procedures differ for different choices of the model potential, (ii) to devise efficient Monte Carlo procedures for the generation of equilibrated configurations of single chains, from which the desired information on $P_n(l)$, $P_n(\vartheta)$ can readily be obtained.

The most detailed model which we have studied is also used by Rigby and Roe,¹⁵ where both bond length and bond angle fluctuations are included, the torsional potential taken is that of Ryckaert and Bellemans,¹⁶ and "nonbonded" interactions between segments separated by more than three bonds along the chain backbone are described by a truncated Lennard-Jones 6-12 potential. The total Hamiltonian thus is, for a chain of N segments

$$\begin{aligned} \mathcal{H} = & \frac{f_b}{2} \sum_{i=2}^N (l_i - l_0)^2 + \frac{f_\theta}{2} \sum_{i=2}^N (\cos \Theta_i - \cos \Theta_0)^2 \\ & - f_\phi \sum_{i=1}^N \sum_{n=0}^3 a_n \cos^n \phi_i \\ & + \sum_{i,j} \left[4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \right]. \end{aligned} \quad (1)$$

Thus the chains are modeled [Fig. 2(a)] as sequences of spherical segments (describing CH_2 as united atoms) connected by springlike valence bonds with equilibrium bond length l_0 and spring constant f_b in their harmonic potential. The valence angle Θ between successive bonds is maintained close to the tetrahedral value Θ_0 by a potential harmonic in $\cos \Theta$, with another "spring constant" f_θ . The "torsional" or "dihedral" angle ϕ , defined by three successive bonds, is constrained to lie mainly in *trans* and *gauche* rotational states by a torsional potential [Fig. 2(b)] defined in terms of the constants f_ϕ , $\{a_n, n = 1, \dots, 5 [a_0 \equiv 1]\}$. The 6-12 Lennard-Jones potential is truncated at a distance $r_v \approx 1.5\sigma$. The reason for this unusually short truncation distance (the standard choice¹⁴ is rather $r_v = 2.5\sigma$) is that this choice was

made by Rigby and Roe¹⁵ and we wish to work with exactly the same model here, to allow for a comparison. In addition, this potential acts only on segments separated by more than three bonds along the chain: all these restrictions are symbolically indicated by the prime on the summation sign in Eq. (1). The parameters describing this potential, as well as those for the two other models for polyethylene mentioned below, are collected in Table I.

If one uses the potential Eq. (1) for an isolated long polyethylene chain, the configurations of the chain generated will not correspond to an "unperturbed" chain in a Θ solvent^{1,2,11} or a melt,² but rather one must obtain either a "swollen" configuration relating to a good solvent or a "collapsed" configuration relating to a bad solvent, depending on the temperature chosen. This feature is undesirable, since we want to use the generated information on $P_n(l)$, $P_n(\vartheta)$ for bulk polymeric material, and thus we have simplified Eq. (1) by setting $\epsilon = 0$ to obtain ideal chain configurations. The effect of including a suitable restricted Lennard-Jones interaction will be studied in a later publication. Note also that any specific effects relating to the fact that the end groups of the chain are $-\text{CH}_3$ — rather than $-\text{CH}_2$ — are completely ignored, as done in Ref. 15.

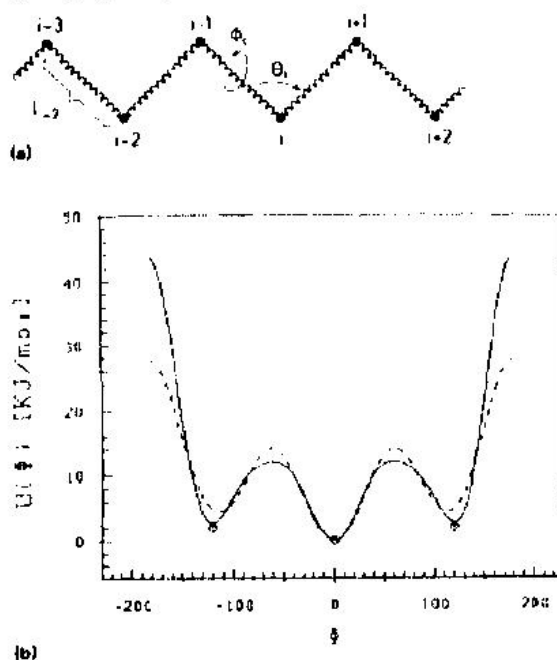


FIG. 2. (a) Schematic model of the polyethylene chain molecule. The spherical segment (labeled by index $i = 1, \dots, N$) denotes a CH_2 unit. The segments are connected by harmonic bonds, the bond length being l_i . Three successive segments define a bond angle Θ_i , and four successive segments a torsional angle ϕ_i (which is zero in the planar all-*trans* configuration shown). It is the angle between the planes formed from the segments $(i-2, i-1, i)$ and $(i-1, i, i+1)$. Segments separated by more than three bonds along the chain (e.g., segments $i-3$ and $i-1$) interact according to a truncated Lennard-Jones potential. (b) Plot of the torsional potential according to the Rigby-Roe model (Ref. 14) (full curve) and according to an *ab initio* calculation (broken curve). The squares correspond to the values of RIS parameters (Table I).